COLLOID CHEMISTRY

by S. Voyutsky

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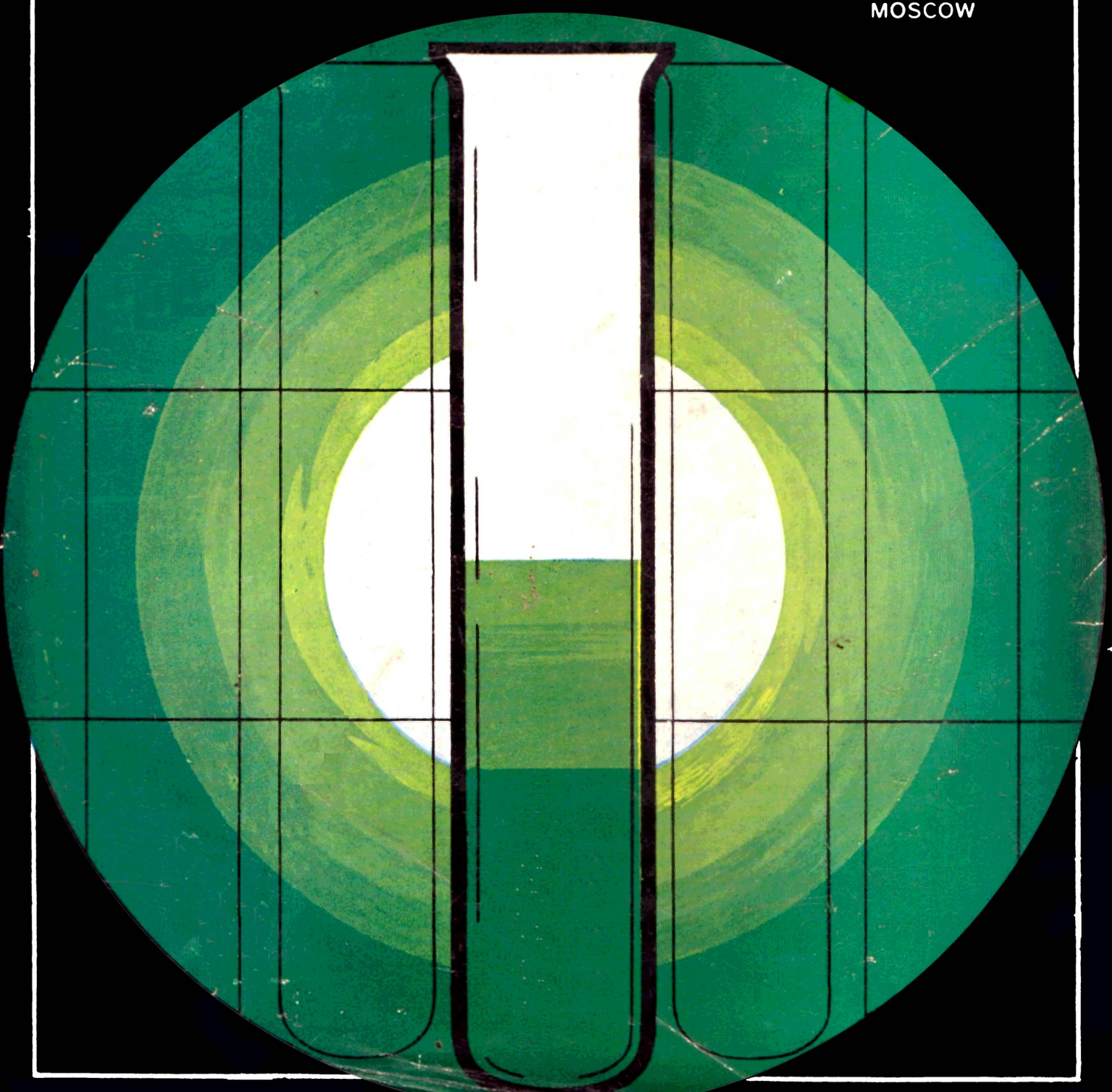

COLLOID CHEMISTRY

This book is a translation of the second edition of the Russian textbook on colloid chemistry for institutes of chemical engineering (the first Russian edition was published in 1964). It explains the general concepts and laws of colloid chemistry and describes the properties of colloidal systems, the methods of investigating them, and the use of colloid chemistry for solving practical problems. The textbook has a chapter on high-molecular-weight substances and their solutions. The Introduction, the chapters on adsorption, and the chapter on the stability and coagulation of colloidal systems have been extensively revised. The book may serve as a textbook for students and postgraduate students of chemical faculties of universities; it will also be of interest to researchers who wish to become acquainted with the modern state of colloid chemistry.

Prof. Sergei Voyutsky, D.Sc. (Chem.), heads the Colloid Chemistry Department of the Lomonosov Institute of Fine Chemical Technology. He specializes in adhesion and in the physico-chemical properties of latices. He has published over 350 articles in Soviet and foreign journals. Prof. Voyutsky is the author of textbooks of colloid chemistry and polymer solutions, and also of monographs, some of which were translated and published in the United States, Japan, Poland and other countries. He is a member of the editorial board of the journals *Kauchuk i rezina* (Caoutchouc and Rubber) and *Kolloidny zhurnal* (Colloid Journal).

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COLLOID CHEMISTRY

by S. Voyutsky

Translated from the Russian by
Nicholas Bobrov

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PREFACE

S. S. Voyutsky's *Colloid Chemistry* has been for many years the main textbook for students of chemical engineering institutes and chemistry faculties of universities in the USSR.

Colloid chemistry has undergone considerable changes since the publication of the first edition. New problems have arisen and new approaches to colloidal phenomena have been found. This includes the concept of disjoining pressure, the formation of colloidal systems as a result of autodispersion, and the presence of periodic structures in colloidal systems. The science of physico-chemical mechanics has greatly developed. All this has made it necessary to considerably work over the textbook by introducing new concepts and, at the same time, deleting outdated material.

I hope S. S. Voyutsky's textbook, written simply and clearly on a high scientific level, will be useful to chemical engineering students and to all those wishing to become acquainted with the problems of modern colloid chemistry.

B. V. Derjaguin

AUTHOR'S PREFACE

More than ten years have passed since the publication of the first Russian edition of this textbook. During this time, colloid chemistry has undergone considerable changes as a result of the work of Soviet and other scientists. Several theoretically interesting and practically important sections are either new or have been greatly expanded, including the concept of stability and coagulation, physico-chemical mechanics, autodispersion, and physical chemistry of aqueous dispersions of rubber (latices).

All this has necessitated a revised edition of the textbook.

As in the first edition, I have sought to bring the material as close as possible to practical problems without making the book a prescription of recipes and a description of the processes of various technological fields. I have tried to present my material clearly, drawing attention mainly to the physical meaning of phenomena.

This textbook of colloid chemistry fits the curriculum of chemical engineering specialties of higher educational institutions, approved by the Educational and Methodological Board of the Ministry of Higher and Secondary Specialized Education of the USSR in 1974. Moreover, it gives information, which will be useful to students and post-graduate students of chemistry faculties of universities. I believe that in this form the book will also be useful to various researchers and engineers working in the field of applied colloid chemistry.

I take this opportunity to express my thanks to the professors and research assistants of colloid chemistry departments of the Moscow State University, the Leningrad State University, the Leningrad Technological Institute, the Moscow Chemical Engineering Institute

and the Moscow Technological Institute of Light Industry, and also to professors G. A. Martynov, A. A. Trapeznikov, G. I. Fuchs and several other persons for their valuable advice on this book. I am especially grateful to the Corresponding-Member of the USSR Academy of Sciences, Prof. B. V. Deryagin (Derjaguin), for his valuable instructions and assistance in writing the textbook.

S. S. Voyutsky

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1

INTRODUCTION. COLLOIDAL SYSTEMS AND THE SUBJECT MATTER OF COLLOID CHEMISTRY

1. CONCEPT OF COLLOIDAL SYSTEMS AND THE DEFINITION OF COLLOID CHEMISTRY AS A SCIENCE

Colloid chemistry was at first only a chapter of physical chemistry, but in the course of time it has grown enormously and become an independent science with its own concepts underlying the interpretation of experimental facts. In addition, special and quite specific colloid-chemistry methods of investigation have been worked out, such as ultramicroscopy, electron microscopy, ultracentrifugation, and electrophoresis. Practice has shown that colloid chemistry is extremely important to modern technology. At present, there is no branch of the economy where colloidal systems and colloidal processes are not used and their methods of investigation are not applied. All this has made colloid chemistry an independent science.

To have a good idea of this science, it is first necessary to know what are colloids and colloidal systems. Man has been acquainted with natural colloidal systems from time immemorial, but it was only comparatively recently that they began to be studied.

In the 1840's the Italian scientist Francesco Selmi drew attention to the anomalous properties of some solutions which, according to modern concepts, are typical colloidal systems. These solutions strongly scatter light; substances dissolved in them precipitate when even very small quantities of salts which do not react with the solute are added to them; dissolution of a substance and its precipitation are not accompanied with a change in temperature and volume of a system, as is the case when crystalline substances are being dissolved. Selmi called such solutions *pseudo-solutions* in order to distinguish them from the ordinary ones. Later, they became known as *sols*.

In the 1860's the English chemist Thomas Graham thoroughly studied the properties of those solutions which interested Selmi. Graham termed these solutions, and the substances which form them, *colloids*, because he believed that glue, or *kolla* in Greek, is their typical representative.

Let us consider the specific features of colloidal solutions that were known as early as the 1860's.

1. All colloidal solutions are capable of scattering light or, in other words, *opalescing*. Opalescence becomes especially noticeable if a beam of converging rays is passed through a colloidal solution, by putting a lens between the light source and the cuvette containing the solution, as Tyndall had done. Under these conditions, a bright glowing cone (the *Tyndall cone*) is seen in the colloidal solution when looking at it sideways. Intensive opalescence is not conclusive proof of the presence of interfaces in a system, but it undoubtedly indicates heterogeneity of colloidal solutions.

2. Diffusion of particles in colloidal solutions is very slow.

3. Colloidal solutions have very low osmotic pressure, which is often even difficult to detect.

The last two properties, i.e., slow diffusion and low osmotic pressure, indicate that colloidal solutions contain relatively large particles of the solute. Indeed, diffusion is affected by the size of particles because, as they grow in size, greater friction makes it more and more difficult for them to move in the solution. Osmotic pressure is a colligative property, i.e., at constant temperature it depends only on the number of particles in the volume, its small value indicates the large size of particles because, at the same gravimetric concentration and the same density of the solute, the larger the particles, the smaller is their amount in the solution.

4. Colloidal solutions are capable of undergoing *dialysis*, i.e., they can be separated, by means of a semipermeable partition (membrane), from the impurities of low molecular weight substances dissolved in them. During dialysis, the molecules of a low molecular weight solute pass through the semipermeable membrane while the colloidal particles which are incapable of passing through the membrane (dialyzing, to use Graham's term) remain behind it as a purified colloidal solution. The ability for dialysis also indicates that the size of particles in colloidal solutions is considerably larger than the size of molecules in true solutions.

The impurities in colloidal solutions can play a very substantial role. In his day, D. Mendeleyev noted that not even a single colloidal solution can be obtained without an admixture of foreign substances, and that all attempts to obtain perfectly pure colloidal solutions had failed. Later, he indicated that some substances, formerly regarded as admixtures, were in the complex composition of colloids. The importance of such impurities, which serve as stabilizers, i.e., substances without which colloidal solutions cannot be obtained, was later revealed by N. Peskov.

5. Unlike true solutions, which are stable systems, colloidal solutions are aggregatively unstable (labile), i.e., a colloid is capable of being separated from a solution (to coagulate) rather readily under

the action of inconsiderable extraneous effects. As a result, a precipitate (*coagulate*) consisting of aggregates of agglomerated primary particles is formed in the colloidal solution. The aggregative instability of colloidal systems is usually the greater, the larger is their concentration. Therefore, typical colloidal systems of sufficient concentration often cannot be obtained.

Among the effects that cause coagulation are heating, freezing, intensive stirring and especially introduction of very small quantities of electrolytes into a solution. Coagulation under the action of electrolytes occurs even when they do not react with the colloid. Hence, coagulation is a physical, not chemical, process.

6. Colloidal solutions can be subjected (not always) to *electrophoresis.* Discovered by F. Reiss in Russia in 1808, this phenomenon consists in the transfer of colloidal particles to one of the electrodes in the electric field. Consequently, colloidal particles, like ions, can carry an electric charge. Contrary to electrolysis where its products are deposited on electrodes in equivalent quantities, in electrophoresis substances are transferred only in one direction. Since Faraday's laws, which quantitatively characterize electrolysis, do not hold in electrophoresis, it was long believed that the two phenomena were not directly connected with each other. In fact, as we will see later, such a conclusion was incorrect.

Colloidal systems may be gaseous, liquid, or solid. At the beginning of this textbook, we will consider mainly colloidal solutions because they have been best investigated and are of great practical importance. Only in the subsequent chapters will we become acquainted with emulsions and foams, and also with gaseous and solid colloidal systems.

Examples of colloidal systems are ordinary water mist, smokes, colloidal solutions of metals (e.g., solutions of platinum, gold, silver), colloidal solutions of silver iodide and arsenic sulphide, solutions of some organic dyes and soaps, milk, and also pumice, ruby glass, opal, cast iron, and some metal alloys.

Colloidal properties may be exhibited by systems consisting of not only inorganic, but also organic substances. Moreover, colloidal systems are widespread in nature and can be obtained in the laboratory. Consequently, the colloidal properties of a system do not depend on its state of aggregation, chemical nature, and origin. How does a colloidal system differ from a non-colloidal one?

Graham believed, at least at first, that colloids differ from ordinary substances (crystalloids) by their nature. Proceeding from this, he divided all substances into two realms: the crystalloid realm and the colloid realm with its special laws. However, he was wrong in his opinion.

A contemporary of Graham's, I. Borshchov, indicated that particles present in colloidal solutions may have a crystalline structure.

Later, at the beginning of this century, the Russian scientist P. Weimarn showed that a substance can possess crystalloid properties under some conditions and produce colloidal solutions under others. For example, colophony forms a true solution when it dissolves in alcohol and a colloidal solution in water. Sodium chloride produces a true solution in water and a colloidal one in benzene. Hence, we would be closer to the truth by saying "the colloidal state of a substance" instead of "the colloidal substance".

Decades of extensive research have shown that the colloidal state of a substance is a highly dispersed (greatly disintegrated) state in which separate particles are not molecules but aggregates consisting of numerous molecules. In accepting this definition of the colloidal state (colloidal system), we may formulate the basic features which distinguish colloidal systems from true solutions. Since colloidal particles consist of numerous molecules, apparently all the thermodynamic properties of a phase may be ascribed to them. Likewise, the molecules of a medium in which colloidal particles are dispersed form another phase. Consequently, unlike true solutions which are homogeneous systems, any colloidal solution is a heterogeneous, multiphase (in the simplest case, two-phase) system and a prerequisite of its formation is the insolubility (or very low solubility) of a substance of one phase in a substance of another one (physical interfaces can exist only between such substances).

Since the components of a system number two or more, colloidal systems are usually multicomponent systems. However, single-component colloidal systems may be formed under certain conditions. An example of these systems, termed *iso-colloidal systems* by Wolfgang Ostwald, are liquids in which molecules form sufficiently large aggregates as a result of the action of molecular forces. Such systems are found rather rarely, and therefore they will not be considered in this textbook.

The accepted definition of colloidal systems is confirmed by the aforementioned properties of colloidal solutions. It is precisely such heterogeneous systems that strongly scatter light, possess low diffusibility, are capable of dialysis, and can be aggregatively unstable.

Solid colloidal systems do not possess all the typical colloidal properties enumerated above. For example, all solid colloidal systems are aggregatively stable under ordinary conditions. This is due only to the enormous viscosity of these systems, which does not allow the particles of a solute to move and form larger aggregates as a result of agglomeration. The aggregative instability of these systems may manifest itself when they melt. Metallic alloys also do not possess opalescence properties. But this is due only to the non-transparency of a metal. Other solid colloidal systems having a clear dispersion medium (e.g., ruby glass, opal) opalesce noticeably. No wonder the term "opalescence" is derived from opal.

Since it follows that any colloidal system is a dispersion of a body (*dispersed phase*) in another one (*dispersion medium*), it would be more correct to speak of colloidal systems rather than colloids.

After this exposition we can define colloid chemistry as a science. **Colloid chemistry is a science of both the properties of and the processes in heterogeneous highly dispersed systems.**

The term "colloid chemistry" is arbitrary. Colloidal systems contain aggregates of molecules, and not simply molecules, as dispersed particles. The most typical process of colloidal systems, coagulation, is the sticking together of the aggregates and formation of yet larger ones under the action of intermolecular, and not chemical, forces. Other processes characteristic of colloidal systems (physical adsorption, electrophoresis, etc.) are also mainly physical or physico-chemical ones. Chemical reactions may occur only when the coagulant interacts with the stabilizer (a substance which forms an adsorption layer on the surface of colloidal particles and ensures the relative aggregative stability of a system). Hence, colloid chemistry is based on two fields of knowledge, i.e., physics and chemistry, the former clearly prevailing, and it is only because of historical traditions that the science of colloidal systems is called "colloid chemistry" instead of the "physical chemistry of heterogeneous highly dispersed systems".

In considering the subject matter of colloid chemistry and colloidal systems, it is necessary to indicate the systems which, while not being colloidal ones in the true sense of the word, were very important to the development of colloid science.

There is a class of very important substances with very large molecules called *high molecular weight compounds* or *polymers*, e.g., proteins, cellulose, rubber, and many synthetic products. The dimensions of macromolecules of these substances may even be greater than the dimensions of colloidal particles in some cases. Then, are the solutions of these substances colloidal systems? It seems that the answer should be yes because, having giant molecules, these solutions possess many properties characteristic of colloidal solutions, e.g., ability for dialysis and low diffusion. However, as recent research has shown, high molecular weight compounds in sufficiently diluted solutions are disintegrated to molecules and, consequently, these solutions are homogeneous systems. Therefore, they cannot be related to typical colloidal systems. To avoid confusion, the solutions of proteins, cellulose, rubber, and other similar substances should be called solutions of high molecular weight substances, and not colloidal solutions as was accepted earlier. The term "solutions of high molecular weight substances" indicates that, first of all, the given systems are true solutions, and, second, they contain giant molecules.

Although the solutions of high molecular weight substances are not colloidal ones in the true sense of the word, the description of their properties is, as a rule, included in the textbook of colloid chemistry because the similarity of several properties of colloidal solutions and of the solutions of high molecular weight substances makes it possible to consider many problems simultaneously for both types of systems. In addition, apart from the typical solutions of high molecular weight substances in which they exist as large, but not interconnected, usually elongated or very loosely coiled molecules, some polymer solutions are essentially the same as colloidal systems. They are solutions of polymers in bad solvents; the chain molecules in such solutions form a compact coil with a distinct surface on which adsorption phenomena may occur. Examples of such systems are natural and synthetic latices whose comparatively large polymer particles are in an aqueous medium and which are stabilized by substances adsorbed on the particle surface. Hence, the difference between classical colloidal systems and polymer solutions is not very pronounced.

Some colloidal systems may originate spontaneously although this seems to contradict the fact that the interface and, consequently, the free energy of a system increase when colloidal systems are being formed. Such systems which undoubtedly have a colloidal nature owing to the large dimensions of particles were detected and studied by P. Rehbinder and his school in the Soviet Union, and now physico-chemists working in the field of colloid chemistry are taking a keen interest in them. These systems include critical emulsions which originate spontaneously at a nearly critical temperature, emulsions of hydrocarbons with a high emulsifier content, and some inorganic disperse systems. The spontaneous formation of colloidal systems and the nature of polymer solutions which are of a clearly pronounced colloidal character will be discussed in Chaps. 8 and 14.

2. MEASURE OF DISPERSION

The measure of disintegration of any disperse system may be: (1) the cross-sectional size of particles a (for spherical particles, the diameter d; for particles having the form of a cube, the cube edge l); (2) its inverse quantity $D = 1/a$, known usually as the *degree of dispersion*; (3) the specific surface area s_{sp}, i.e., the area of interface per unit volume of the dispersed phase. All these quantities are interconnected. The smaller the dimensions of particles, the greater is the degree of dispersion or the specific surface, and vice versa.

Colloidal systems are those whose value a is within the limits of 1-100 nm (10^{-7}-10^{-5} cm) while the degree of dispersion is within the limits of 1-100 nm^{-1} (10^{7}-10^{5} cm^{-1}). The upper limit of the degree of

dispersion of colloidal systems is due to the fact that, on further granulation of a substance, a solution no longer contains aggregates of molecules but individual molecules ~ 0.1 nm in size. The lower limit of the degree of dispersion of colloidal systems is determined by a sharp reduction in the velocity of thermal motion of particles whose cross-sectional size is more than 100 nm. Notwithstanding the established limit of 100 nm, disperse systems of even greater coarseness whose particle size may reach several micrometres and sometimes considerably more are treated in the textbook of colloid chemistry. This is expedient because such systems, known as microheterogeneous systems, whose particles are easily visible under the microscope, have many properties in common with colloidal or, in other words, ultramicroheterogeneous systems whose particles are not visible under the microscope. Among microheterogeneous systems are powders, suspensions, emulsions, foams, and several other systems, which are of great practical importance.

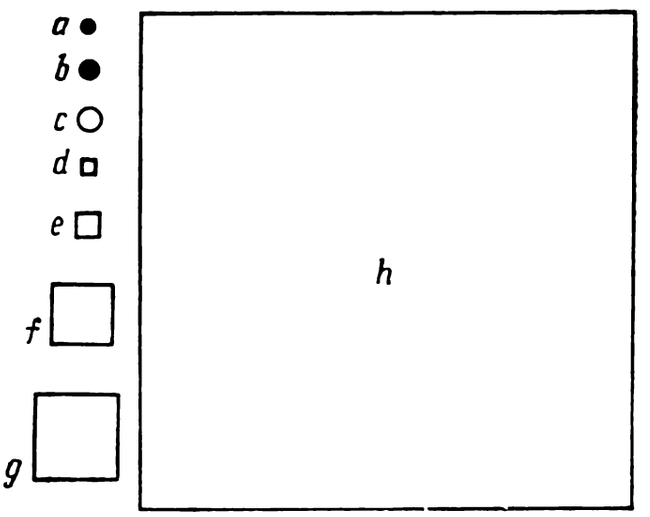

Fig. 1.1. Proportion of dimensions of colloidal particles and molecules: *a*—hydrogen molecule, diam.= 0.1 nm; *b*—chloroform molecule, diam.= 0.8 nm; *c*—hemoglobin molecule, diam.= 2.5 nm; *d*, *e*, *f*, *g*, *h*—particles of a gold sol which correspond to diam.= 1 nm, 3 nm, 10 nm and 15 nm, and sedimenting particles

Fig. 1.1 represents the proportion of the dimensions of particles of a gold sol and some molecules. It shows that fine colloidal particles may be smaller than the molecules of a high molecular weight substance (e.g., hemoglobin) and only a little larger than the molecules of a low molecular weight substance (e.g., chloroform).

It is precisely the comparatively small size of colloidal particles that determines the similarity of some properties of colloidal systems and true solutions. On the other hand, the relatively large dimensions of particles of colloidal systems determine their inability to penetrate through the semipermeable membrane, low diffusibility, and the ability to sediment in a sufficiently powerful field of an ultracentrifuge. The specific features of colloidal systems that are connected with the dimensions of particles will be considered in greater detail in Chap. 3 which is on the molecular-kinetic properties of colloidal systems.

Speaking of the size of particles of colloidal systems, two circumstances should be taken into account.

First of all, the concept "cross-sectional size" makes sense for spherical particles and probably also for cubic particles. If particles

greatly differ in shape from a sphere, their size depends on the direction in which measurement is made. However, particles are equated to spherical ones very often in colloid chemistry, assuming that these spherical particles act in exactly the same way as true particles in a certain respect. The diameter of such a conventional spherical particle is known as the *equivalent diameter.*

Secondly, particles are rarely of the same size in colloidal systems. Systems with particles of the same size, known as *monodisperse* systems, may be prepared only artificially by special techniques. Most colloidal systems are *polydisperse*, i.e., they contain particles of different dimensions.

The specific area s_{sp} of a disperse system is expressed by the equation

$$s_{sp} = s_{1,2}/V \tag{1.1}$$

where $s_{1,2}$ = surface area between phases 1 and 2 (interface);
V = total volume of the dispersed phase.

It is not difficult to calculate the specific area of a disperse system if the size and shape of particles are known. Taking into account that the specific area is numerically equal to the ratio of the surface of a particle $s_{1,2}$ to its volume v_1, we have for the system containing cubic particles with edge l

$$s_{sp} = s_{1,2}/v_1 = 6l^2/l^3 = 6/l \tag{1.2}$$

For a system containing spherical particles with radius r, we obtain

$$s_{sp} = s_{1,2}/v_1 = 4\pi r^2/(^4/_3\pi r^3) = 3/r = 6/d \tag{1.3}$$

In general, we have

$$s_{sp} = s_{1,2}/v_1 = k \cdot 1/a = kD \tag{1.4}$$

where k = coefficient which depends on the particle shape.

By (1.4), the specific area is directly proportional to the degree of dispersion D and inversely proportional to the particle size a.

As a colloidal system becomes more dispersed, its specific area sharply increases. This is seen in Table 1.1 which shows the change in the specific area of 1 cc of a substance when it disintegrates into cubes of smaller dimensions.

By their specific area, colloidal systems differ from other disperse systems. Indeed, molecular systems, e.g., true solutions, cannot be characterized by the specific area because molecules do not have

Table 1.1. **Change in s_{sp} upon Disintegration of 1 cc of a Substance**

l, cm	Number of cubes	Volume of a cube v_1, cc	Surface area of a cube $s_{1,2}$, cm^2	$s_{sp} = s_{1,2}/v_1$
1	1	1	6	6
1×10^{-1} (1 mm)	1×10^{3}	1×10^{-3}	6×10^{-2}	6×10^{1}
1×10^{-2}	1×10^{6}	1×10^{-6}	6×10^{-4}	6×10^{2}
1×10^{-3}	1×10^{9}	1×10^{-9}	6×10^{-6}	6×10^{3}
1×10^{-4} (1 μm)	1×10^{12}	1×10^{-12}	6×10^{-8}	6×10^{4}
1×10^{-5}	1×10^{15}	1×10^{-15}	6×10^{-10}	6×10^{5}
1×10^{-6}	1×10^{18}	1×10^{-18}	6×10^{-12}	6×10^{6}
1×10^{-7} (1 nm)	1×10^{21}	1×10^{-21}	6×10^{-14}	6×10^{7}

a surface in the ordinary sense of the word. At the same time, the specific area of coarsely dispersed systems is very small. Only heterogeneous highly dispersed colloidal systems have a well developed surface. This is clearly shown in the diagram (Fig. 1.2) which represents a change in the specific surface area with a change in the particle size from coarsely dispersed systems to systems having a molecular degree of dispersion. The curve $s_{sp} = f(a) = k/a$ has the form of an equilateral hyperbola. To the right, in the region of coarsely dispersed systems, the curve asymptotically approaches the abscissa. To the left, it breaks off when colloidal particles become as large as molecules and the interface disappears. Of course, the boundary between the colloidal and molecular degrees of dispersion cannot be established exactly; for individual systems, it may shift to the right or to the left depending on the chemical nature of a dispersed phase and the dispersion medium.

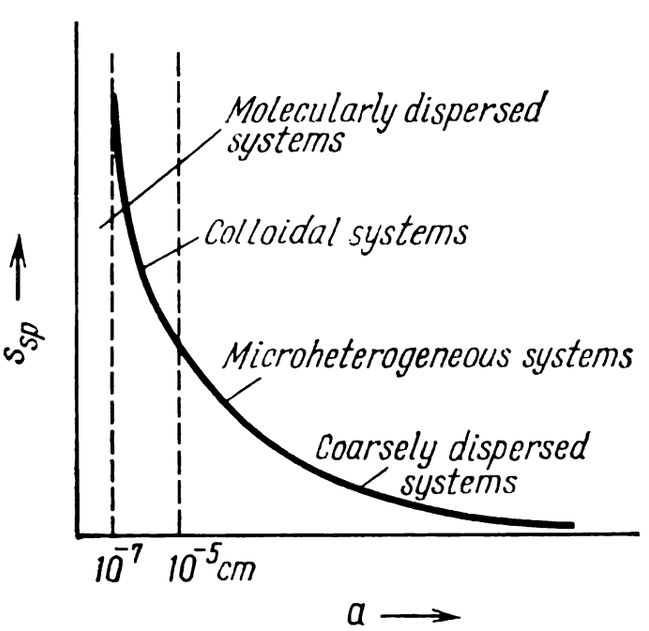

Fig. 1.2. Dependence of the specific surface area of a system on the particle size

The transition from coarsely dispersed to molecularly dispersed systems is a continuous process; however, colloidal and microheterogeneous systems which hold an intermediate place are qualitatively quite specific. Since these systems have a large specific area

adsorption and, in general, surface phenomena are very important to them, while the behaviour of coarsely dispersed and molecular systems is determined mainly by their bulk properties.

3. HETEROGENEITY OF COLLOIDAL SYSTEMS AS THEIR BASIC DISTINCTION FROM MOLECULAR SOLUTIONS

We have already seen that aggregate instability is a feature of colloidal systems. This property is of great practical importance. It would not be an exaggeration to say that the main job of a production engineer of a process in which colloidal systems are involved is either the maintenance of the aggregative stability of a system or, conversely, the ensurance of certain coagulation conditions.

Aggregative instability is the central problem of colloid chemistry; it is necessary to consider at the very beginning of the textbook what determines the aggregative instability of colloidal systems and why many of them exist for a very long time, notwithstanding their fundamental aggregative instability. The causes of the instability of colloidal systems may be explained from two standpoints, i.e., thermodynamically and kinetically.

According to thermodynamics, the aggregative instability of colloidal systems is caused by the rather great and always positive free surface energy which is concentrated on the interface of a system. Since surface energy is free energy and all systems that have surplus free energy are unstable, this determines the coagulability of colloidal systems. In coagulation, particles adhere, the interface at least partially disappears, and thus the free energy of a system decreases. In fact, M. Smoluchowski and recently G. Martynov have drawn attention to the fact that, for the free energy of a system to diminish, particles do not have to be in direct contact. Free energy may diminish also when particles approach one another only to a distance that allows them to interact through the layer which divides their media.

Indeed, let

$$F = s_{1,2} f \tag{1.5}$$

where F = free surface energy of the entire system;
$s_{1,2}$ = area of interface;
f = specific free surface energy.

The quantity f is the sum of the interfacial energy f_a, determined by the state of the monolayer at the interface, and the free energy f_v near the surface, i.e., $f = f_a + f_v$. The volume-surface contribution of f_v is determined by a change in the state of liquid layers near

the interface. Notwithstanding that generally $f_a \gg f_v$, the stability of a system is in most cases precisely connected with a change in f_v since the interface usually does not disappear when aggregates are formed from solid particles. Therefore, in the course of coagulation, the quantity f_a remains practically constant while f_v changes, the extent of the change depending on the diminution of the distance between particles. Of course, all this does not apply to emulsions where particles coalesce with the complete elimination of the interface that initially separated the particles.

Since colloidal systems which have a large surface area and high free energy are as a rule non-equilibrium systems, the well-known phase rule is inapplicable to them. Such systems will apparently always tend to an equilibrium state which corresponds to the division of a system into two separate phases with a minimum interface although this equilibrium may practically never set in. The thermodynamic interpretation of the causes of stability or instability of colloidal systems is extremely simple. However, like any thermodynamic interpretation, it is a formal explanation, i.e., it does not reveal the essence of the property of aggregative instability. Moreover, thermodynamics does not establish a connection between the free energy of a system and the duration of the non-equilibrium state of a system. Therefore, the explanation of aggregative instability or stability of colloidal systems from the standpoint of physical kinetics is more comprehensive in this case.

According to kinetic concepts, the instability or stability of a colloidal or microheterogeneous system is determined by the balance of forces acting between its particles. Such forces are of two kinds: (1) adhesive or attractive forces which tend to bring particles closer together and form aggregates from them, and (2) repulsive forces which hinder coagulation.

Adhesive forces usually have the same nature as intermolecular (van der Waals) ones. The forces which act between particles grow very rapidly when particles are brought closer to one another.

Repulsive forces may be electric ones which originate as a result of the selective adsorption by the interface of one of the electrolytic ions present in a system. Since the particles of a dispersed phase are by their nature the same and always adsorb the same ion, they all acquire an electric charge of the same sign and experience mutual repulsion; this prevents them from approaching one another to such a distance at which considerable attractive forces may act. Another cause that prevents colloidal particles from approaching one another to this distance may be the formation of a solvate shell from the molecules of the medium on the particle surface. Such a shell originates as a result of the adsorption of either the molecules of the medium or the molecules or ions of the third component (stabilizer) of a system by the dispersed phase. Apart from these two fac-

tors, there are also other factors which ensure the aggregative stability of colloidal systems; they are considered in detail in Chap. 9.

Hence, the relative stability of a colloidal system is determined by whether the repulsive forces are great enough to prevent particles from closely approaching one another. Of course, such an explanation does not contradict the fundamental instability of most colloidal systems because adhesive forces are as a rule greater than repulsive forces when the particle surfaces are in the immediate proximity, and two particles would gain energetically if they form an aggregate. We will see later that there are many ways of reducing repulsive forces; in particular, one such technique is the introduction of electrolytes into a system.

4. DISJOINING PRESSURE *

As the layer of a liquid which separates the surfaces of two solids or, in general, any two phases that have adsorbed ions grows thinner, two kinds of interaction forces originate between the surfaces of these phases. First, there are forces which depend on attraction between molecules of both bodies, between molecules of a liquid, and between molecules of a liquid and each body (or phase). If both bodies are the same, these forces cause the attraction of bodies that tends to thin the liquid interlayer. Second, as a result of the action of electric forces, repulsion always originates between the same bodies, causing the liquid interlayer to thicken. Therefore, for the interlayer thickness to remain unchanged and for the system as a whole to maintain thermodynamic and simultaneously mechanical equilibrium, additional force should be applied to the surfaces of the interlayer, a force which in the first case tends to thicken it and, in the second, thin it. If both bodies (phases) are solid, these forces can be applied directly to them. If the phases are liquid or gaseous and are separated by a liquid partition, equilibrium can be maintained by changing pressure in them.

In both cases, this additional force counterbalances pressure in the thin interlayer. Consequently, the equilibrium value of pressure differs from the value of pressure which was in the interlayer prior to thinning and which is maintained in the volume of the liquid phase. Surplus pressure revealed by the interphase liquid interlayer when it is sufficiently thinned is known as *disjoining pressure* and denoted by the symbol $\Pi(h)$. The concept of disjoining pressure was introduced by B. Deryagin in 1935. The measure of the quantity $\Pi(h)$ is the difference between p_1, pressure on the layer that is

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* This section was written by B. Deryagin.

plane-parallel from the side of the phases that limit it, and p_0, pressure of the phase from which the layer was formed and with which it communicates along the perimeter:

$$\Pi(h) = p_1 - p_0$$

The function $\Pi(h)$ has different forms for diverse phases and interlayers, indicating the patterns of a change in the forces of interaction between them with a change in the interlayer thickness.

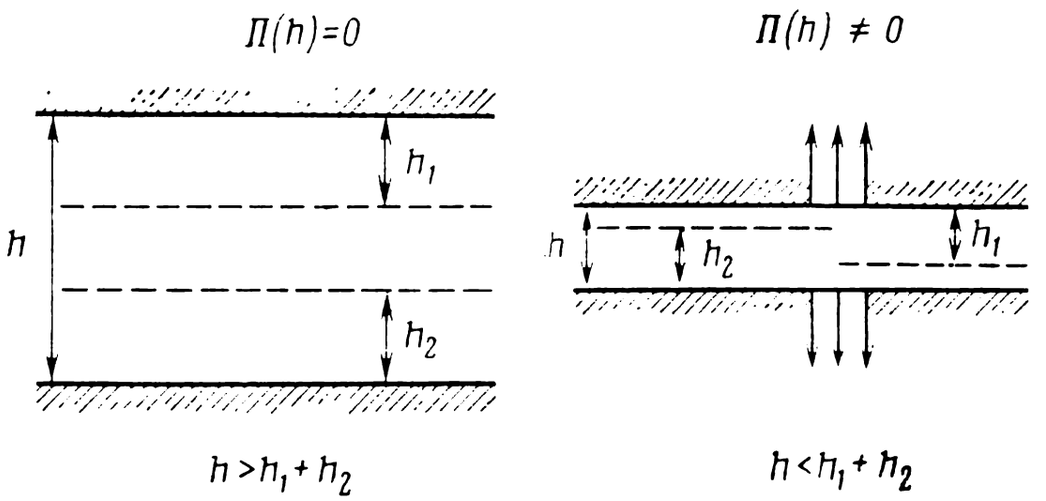

Fig. 1.3. Diagram explaining the origin of disjoining pressure when the boundary layers having a thickness of h overlap. The arrows denote the forces of disjoining pressure when it is positive

The function can be calculated theoretically only for definite cases and with limited precision. Therefore, the methods of experimentally determining the quantity Π are of special importance.

Disjoining pressure was studied by B. Deryagin and coworkers by making direct measurements. At first, they discovered and studied disjoining pressure for liquid interlayers between solid plane surfaces, and then for wetting films on different surfaces. Later, the disjoining pressure of films of solutions of soaps and other surfactants placed between two gaseous media (bubbles) was discovered and investigated. These investigations were continued by D. Haydon, A. Corkill, and other scientists.

A contribution to disjoining pressure may be made by the van der Waals forces (the molecular component of disjoining pressure) and electric forces (the ionic-electrostatic component). In addition, B. Deryagin, N. Churayev, Z. Zorin, and others have shown the existence of the third, "structural" component of disjoining pressure. It originates when the thickness of the interlayer h (Fig. 1.3) becomes less than the total thickness $(h_1 + h_2)$ of its boundary layers where molecules are ordered contrary to their random arrangement in the liquid volume. When $h < h_1 + h_2$, then apparently a part of the structurally changed layers that limit the interlayer are pressed out into the liquid volume and their ordered structure is des-

troyed, which requires work. According to the first law of thermodynamics, when the layer is thinned, work should be done to overcome additional, i.e., in this case disjoining, pressure.

In applying the first law of thermodynamics, we assume the process of interlayer thinning to be so slow that the dissipation of energy and work done to overcome liquid viscosity can be neglected. Disjoining pressure is unrelated to viscosity and other mechanical properties of a liquid. Disjoining pressure may be either positive or negative.

5. EFFECT OF THE DEGREE OF DISPERSION ON THE PROPERTIES OF DISPERSE SYSTEMS

Many properties of disperse systems depend on the degree of their dispersion. Some of them, e.g., diffusibility and osmotic pressure, are exhibited more strongly in highly dispersed systems. Conversely, other properties, e.g., sedimentation of particles, become more noticeable in coarsely dispersed systems. The following properties are displayed at intermediate degrees of dispersion which correspond to particles of colloidal dimensions: light scattering, the intensity of colour of colloidal systems, the covering ability of pigments, the action of fillers in raw rubbers, and so forth. Even the hardness of alloys which are a complex system of extremely fine crystalline particles is maximum when these particles have colloidal dimensions. There is evidence that catalytic action also is exhibited most strongly by catalysts which are characterized by the colloidal extent of dispersion.

Notwithstanding the undeniable connection between the particle size and the properties of a disperse system, it is wrong to attribute all the specific features of a disperse system only to the degree of dispersion as this was done, for example, by the German scientist W. Ostwald. Proceeding from the assumption that the size of particles was pre-eminent among all the other properties, Ostwald even proposed to call the science of colloidal systems not colloid chemistry but dispersoidology, i.e., the science of the dispersed state of matter. Soviet scientists, especially N. Peskov, indicated that such a view was one-sided and represented a purely mechanical approach. Dispersoidology reduced everything only to a decrease or increase in the particle size and took no account either of the complex interaction between the particles of the dispersed phase and those of the dispersion medium that was accompanied by adsorption in most cases, or of the possibility of purely chemical interactions in coagulation. But these phenomena play an important part in colloidal systems. According to dispersoidology all disperse systems are qualitatively identical and differ from one another only by the

particle size; dispersoidology could not explain the special properties by which colloidal systems differ from both molecularly dispersed and coarsely dispersed systems.

Lastly, the untenability of dispersoidology was clearly revealed after a detailed investigation of the nature of polymer solutions. According to Ostwald and other advocates of dispersoidology, all colloidal properties must necessarily be exhibited by systems containing particles of colloidal dimensions. However, as we have already seen, the solutions of high molecular weight substances whose molecules are of colloidal dimensions exhibit only some properties typical of colloidal systems (optical, molecular-kinetic properties); as regards other properties, they have very little in common with typical colloidal solutions.

In explaining the properties of a colloidal system, it is necessary to take into account not only the particle size but also the presence of the interface which makes it possible for various adsorption phenomena to occur, and also different chemical reactions that may take place on the particle surface.

6. CLASSIFICATION OF COLLOIDAL AND MICROHETEROGENEOUS SYSTEMS

As in any science which is concerned with numerous objects, in colloid chemistry it is necessary to classify colloidal and microheterogeneous systems in order to understand their diversity. Although many suggestions have been made, a single classification of these systems does not yet exist because any proposed classification takes only one property of a disperse system, instead of all, as a criterion. Hence, as N. Peskov has observed, regardless of the classifications we accept, there will always be individual cases when an accepted classification is contestable or even inapplicable.

Let us briefly consider the classifications which have become most popular.

Classification according to the degree of dispersion. Siedentopf and Zsigmondy suggested calling particles visible under the microscope, i.e., particles whose dimensions are greater than its resolving power (0.2 μm), "microns", and colloidal particles invisible under the microscope, "ultramicrons". These authors divided ultramicrons into submicrons, i.e., particles of 5-200 nm that are detected by means of the ultramicroscope, and amicrons, i.e., particles smaller than 5 nm that are not detected even under the ultramicroscope. They classified not disperse systems proper, but the particles contained in them. There are no objections to this, but attempts to

use their principle for classifying colloidal and microheterogeneous systems have failed.

Indeed, as we have seen, the degree of dispersion is only one of the factors that determine the properties of a system; consequently, the characteristics of disperse systems according to the size of particles contained in them will be incomplete and one-sided. Moreover, monodisperse systems are found very rarely in practice, and the classification cannot be applied to polydisperse systems. Lastly, in connection with the aggregation phenomena that occur in colloidal systems, the size of particles contained in them may change, and thus the same system would have to be related to different classes at different times of its existence.

Classification according to the state of aggregation of the dispersed phase and the dispersion medium. This classification was proposed by Wolfgang Ostwald. There can be nine combinations of the dispersed phase and the dispersion medium in their different states (Table 1.2). However, only eight combinations can be realized in practice because gases under ordinary conditions dissolve in one another and form a homogeneous system.

Table 1.2. **Classification of Disperse Systems According to the State of Aggregation of the Dispersed Phase and the Dispersion Medium**

Dispersed phase	Dispersion medium	Conventional notation for a system	Name of a system
Gas	Gas	G/G	(Colloidal system cannot exist)
Liquid	Gas	L/G	Mists
Solid	Gas	S/G	Smokes, dust
Gas	Liquid	G/L	Foams
Liquid	Liquid	L/L	Emulsions
Solid	Liquid	S/L	Colloidal solutions, suspensions
Gas	Solid	G/S	Solid foams, porous bodies
Liquid	Solid	L/S	Solid emulsions
Solid	Solid	S/S	Solid sols, alloys

In colloid chemistry, all the systems which correspond to the colloidal extent of dispersion are known as *sols*. Therefore, the L/G and S/G systems have the common name of *aerosols*. This is a conventional name because the dispersion medium of aerosol may be not only air, but also any other gas.

Systems with a liquid dispersion medium, denoted as G/L, L/L and S/L, are known as *lyosols* (from the Greek word "lyein" meaning "to dissolve"). Lyosols are divided into *hydrosols*, *alcosols*, *etherosols*, and *benzosols*, depending on the nature of the dispersion medium (water,

alcohol, ether, and benzene, respectively). Colloidal systems whose dispersion medium is organic liquid are known as *organosols.* In colloid chemistry, microheterogeneous systems having a solid dispersed phase and a liquid dispersion medium are usually known as *suspensions.*

Classification according to the state of aggregation of the dispersed phase and the dispersion medium is very convenient for generalizing the entire diversity of colloidal systems, and probably now it is the most widely accepted classification. We will also adhere to this classification to a certain extent in our textbook. However, it has a rather great flaw: as the particle size diminishes, the difference in the state of aggregation of the dispersed phase gradually evens out in different colloidal systems. Thermodynamically we can hardly speak of the state of aggregation of particles whose cross-sectional size is several angstroms and which consist of a comparatively small number of molecules. This is borne out by experiment which shows that sols for whose preparation substances in the liquid and solid states were used as the dispersion medium cannot be distinguished from one another by the properties of highly dispersed systems.

Proceeding from this, Zsigmondy simplified Ostwald's classification, taking only the state of aggregation of the dispersion medium as the criterion of classification. Then, Ostwald's eight possible classes are reduced to three, i.e., to systems having gaseous, liquid, and solid dispersion media.

Classification according to the interaction of the dispersed phase and the dispersion medium. This classification is suitable only for systems with a liquid dispersion medium, but not for systems having a gaseous or solid dispersion medium.

Zsigmondy proposed classifying colloidal solutions by the ability of a dry residue obtained as a result of carefully evaporating a liquid to dissolve in a pure dispersion medium. He termed systems whose dry residue was incapable of spontaneously dissolving in the dispersion medium *irreversible colloidal systems.* They include typical colloidal solutions: lyosols of metals, hydrosols of silver iodide and arsenic sulphide, and so forth. He applied the term *reversible colloidal systems* to systems whose dry residue on contact with the medium usually swells at first and then spontaneously dissolves and forms a colloidal system again (solutions of gelatin in water or of rubber in benzene).

A comparison of the systems representing these classes has shown that they possess also other properties which distinguish them from one another. Irreversible colloidal systems have signs of colloidal solutions: it is difficult to obtain them with a high content of the dispersed phase; they readily coagulate when electrolytes are intro-

duced into them and form compact precipitates which contain a small amount of the dispersion medium. On the contrary, reversible colloidal systems of a sufficiently high concentration may be obtained; they are far less sensitive to electrolytes while the precipitates formed upon addition of a large amount of the coagulant to a sol are very bulky, viscous, and contain much dispersion medium.

Freundlich argued that the reversibility or irreversibility of a colloidal system is determined by the interaction between the dispersed phase and the dispersion medium. Molecules of the dispersed phase of reversible colloids react with molecules of the dispersion medium, the former being able to dissolve in the latter. Proceeding from this Freundlich suggested calling such colloidal systems *lyophilic colloidal systems* (from the Greek words, "lyein" meaning "to dissolve" and "philein" meaning "love"). The dispersed phase of irreversible colloids is incapable of reacting with the dispersion medium and, consequently, dissolving in it. Therefore, Freundlich called these systems *lyophobic* ones (from the Greek word "phobos" meaning "fear"). In some manuals, irreversible or lyophobic colloidal systems are also called *suspensoids* while reversible or lyophilic systems are called *emulsoids* because some of their properties are similar to those of suspensions or emulsions. When the dispersion medium of a system is water, these two classes can be called *hydrophilic* and *hydrophobic systems*, respectively (from the Greek word "hydōr" meaning "water").

Evidently, while irreversible or lyophobic colloidal solutions are typical colloidal systems, reversible or lyophilic systems are solutions of high molecular weight compounds. Indeed, only substances which disintegrate into individual, very large molecules are capable of spontaneously dissolving in a dispersion medium and producing solutions having colloidal properties. Such substances are compounds of high molecular weight. Typical colloidal systems having an interface as a rule cannot be formed spontaneously because this contradicts thermodynamics.

The spontaneous formation of colloidal systems, and the formation of heterogeneous polymer solutions will be treated in Chaps. 8 and 14. Zsigmondy and Freundlich erroneously related polymer solutions to colloidal ones, because it was not established then that these were true solutions.

Hence, Zsigmondy's and Freundlich's classification is in essence a classification of not colloidal systems but disperse systems which contain particles corresponding to colloidal dimensions; this classification includes both typical colloidal systems and polymer solutions.

It is pertinent to note in this respect that, together with typical irreversible and reversible systems, there are, according to Zsigmondy's and Freundlich's classification, intermediate systems which

are difficult to relate to one of the two classes. They are, for example, sols of hydroxides of some metals: $Al(OH)_3$, $Fe(OH)_3$, $Sn(OH)_4$. Investigation by optical methods shows that these systems contain colloidal particles (aggregates of molecules). There are also other grounds for regarding these systems as heterogeneous ones. At the same time, these systems are reversible; they may be obtained with a sufficiently large concentration of the dispersed phase, and they are less sensitive to electrolytes than typical lyophobic systems. Such properties of these systems are usually said to be due to the exceptionally high hydration of the particles in them. However, several investigators now believe that the dispersed phase in these systems may be in the form of either colloidal particles or macromolecules, depending on the technique used. The nature of these solutions is still not completely clear. We will return to this in Chaps. 9 and 14.

Recently, some Soviet scientists began giving the term "lyophilic colloidal systems" a meaning which essentially differed from that given to it earlier. For example, on P. Rehbinder's proposal, the term "lyophilic sols" began to be applied not to solutions of high molecular weight compounds but to colloidal systems in equilibrium formed under definite conditions as a result of the spontaneous disintegration of the dispersed phase to particles of colloidal dimensions. Such a name is quite justified because particles in such systems have colloidal dimensions and react with the dispersion medium, i.e., they are lyophilic to it.

Some scientists propose applying the term "lyophilic" to sols which have acquired aggregative stability owing to adsorption of non-ionogenic surfactants on the surface of their particles. Such sols differ from ion-stabilized colloidal systems by high resistance to the action of electrolytes because the surface of particles of the dispersed phase became lyophilic upon adsorption of molecules of non-ionogenic surfactants.

Classification according to interaction between particles. According to this classification, disperse systems are divided into *freely dispersed* and *coherently dispersed* ones.

Freely dispersed systems are structureless systems in which the particles of the dispersed phase are not bound into a continuous network and are capable of moving freely in the dispersion medium under the action of gravity or Brownian motion. Such systems do not offer resistance to shear, they possess fluidity, and all the other properties characteristic of ordinary liquids. They are lyosols, sufficiently diluted suspensions and emulsions, and aerosols.

In coherently dispersed systems, the particles are bound with one another by intermolecular forces, forming peculiar three-dimensional networks or frames in the dispersion medium. Particles which

form the structure are apparently incapable of moving reciprocally, and can only oscillate. Such systems are gels, concentrated suspensions (pastes), concentrated emulsions and foams, and powders. Gels can be produced as a result of coagulation of colloidal systems and precipitation (coagels), and also by formation of molecular bonds between sol particles to yield comparatively loose networks or frames (lyogels). In the latter case, external homogeneity of a system is maintained in gels. The transition of a sol to the state of a gel is known as *gelation*. Of course, gelation is always promoted by a higher concentration of the dispersed phase in a system.

Coherently dispersed systems which to a certain extent possess properties of a solid should not be confused with systems having a solid dispersion medium. The particles of the latter systems are also incapable of moving in respect of one another but the cause of this is essentially different, i.e., the enormous viscosity of the dispersion medium.

The given classification is applicable not only to colloidal systems but also to systems which are solutions of high molecular weight substances.

7. IMPORTANCE OF COLLOIDAL SYSTEMS AND COLLOIDAL PROCESSES IN NATURE AND ENGINEERING

Extremely widespread in nature, colloidal systems are also very important in modern engineering. Some examples showing the role of colloidal systems and colloidal processes in our environment are given below. Many other examples which show the role of colloid chemistry in man's everyday activity will be given while presenting the material contained in this textbook.

Colloidal systems and colloidal phenomena are observed far beyond the Earth. Interstellar matter consists mainly of gases and dust; observations of light absorption have shown that the size of dust particles in outer space is usually not more than 3×10^{-5} cm, i.e., the particles have typical colloidal dimensions.

Comets—gas-and-dust clouds—are thus enormous colloidal systems while the characteristic glow of comets that originates upon the illumination of very fine particles by sun rays is merely a manifestation of light scattering. It is still not clear why comets exist for a long time: whether owing to the enormous rarefaction of the cosmic gas-and-dust clouds and rare encounters of particles with one another, or to the relative aggregative stability of a system that is determined by some factor, e.g., the electric charge of particles that may originate as a result of the adsorption of ions by dust particles. It has now been established that outer space contains large quan-

tities of ions produced by the action of various radiations on gas molecules.

The origin of the solar system or, at least, planets around the Sun is also directly connected with colloidal phenomena, as Arrhenius had observed. According to the cosmogonic concepts of H. Urey and V. Fesenkov, the solar system was formed from a gas-and-dust substance. According to one of the theories of the formation of planets that was elaborated by O. Schmidt, planets originated from a gas-and-dust cloud captured by the Sun. The space of our Galaxy has many such clouds, and there are no grounds for assuming that the preplanetary cloud of matter surrounding the Sun greatly differed by its composition from galactic clouds, regardless of its origin.

O. Schmidt proved his theory by the fact that planets have almost circular orbits. Planets with such orbits could be formed only by the combination of a large number of bodies contained in the gas-and-dust cloud which formerly moved along independent elliptic orbits around the Sun. He did not thoroughly consider the mechanism of combination of dust particles but it may be assumed that an important part here is played by the same factors as those in the agglomeration of aerosol particles. Undoubtedly, the formation of aggregates should be affected by surface forces, electric charges on the particles, and so forth. Of course, everything is greatly complicated by the fact that the gas-and-dust cloud is strongly acted upon by such a powerful factor as solar radiation in all its forms.

Colloidal systems and processes are very important in meteorological phenomena, the formation of rocks and minerals, and in agriculture.

Clouds and mists are colloidal systems of the L/G type, and their particles often carry an electric charge. Rain, lightning, and other meteorological phenomena should be regarded as phenomena connected with colloidal processes.

As a result of the thorough investigation of aerosol properties by B. Deryagin, N. Fuchs, I. Petryanov, A. Amelin, and other Soviet scientists, there are now techniques of counteracting dusts, smokes and mists, and techniques of artificially causing rain, extremely important in agriculture.

The formation of deltas when rivers flow into the sea is also largely a colloidal process. The fresh water of rivers usually contains an enormous number of suspended mineral particles whose dimensions are similar to colloidal ones. Like most colloidal particles, these particles are electrically charged. When rivers flow into the sea, river water mixes together with sea water which contains a considerable amount of electrolytes and, as a result, the suspended particles lose stability, coagulate and settle to the bottom as aggregates, forming shoals.

Colloid chemistry is very important in agriculture.

Soil is an extremely complex colloidal system. The nature, size and form of soil particles determine the water permeability and absorptivity of soil which in turn influence crop yields. Sands having low degree of dispersion readily pass water through while highly dispersed clays retain moisture well. The presence of alkalis increases the degree of dispersion of soils and makes them more hydrophilic. Conversely, calcium salts coagulate soil and make them less hydrophilic. This is the basis of soil liming which is intended to reduce the ability of soil to retain moisture. Wide use is now made of what are called structuralizing agents based on polymers whose introduction into soil prevents erosion and gives the soil desirable properties.

In the national economy, all industries are more or less connected with colloidal systems and colloidal processes. For example, the metallurgist must obtain metal with an optimum micro- and ultramicrostructure, and this is done by introducing definite additives into an alloy. In the metal-processing industry, such processes as tempering, annealing and rolling are also intended to change the microstructure of a metal in the necessary way.

The ceramic industry is connected very closely with colloid chemistry because its principal raw material, clay paste, is a concentrated suspension of hydrated aluminium silicates. An important fact is that the quality of clay is determined more by the physical properties of its particles (dimensions, shape, surface state) than by chemical ones.

Another way of using clays, but this time as components of solutions employed in drilling, catalysts, catalyst supports, driers, and clarifiers of various liquids, ranging from wine to products of the oil-processing industry, is being worked out by F. Ovcharenko and co-workers in the Ukraine.

The laws of colloid chemistry are very important in the production of new building materials on the basis of mineral raw material. The basic research carried by P. Rehbinder and his school in the field of binders has led to the production of construction materials which are of high strength and possess other valuable properties.

Industries which process organic raw material are also connected with colloid chemistry. For example, paper-making techniques which give valuable properties to paper include the granulation of plant fibre until it is highly dispersed, the preparation of dispersions of various pasting agents (colophony, artificial resins, raw rubber), and the deposition of the particles of these dispersions on the surface of ground fibre as a result of the coagulating action of electrolytes.

Fibre dyeing and leather tanning are also examples of techniques in which colloidal processes play the main role. Dyeing and tanning consist in the diffusion of colloidal particles of the dye or the tan-

ning agent into the fabric or clean rawhide, the coagulation of these particles as they come into contact with elementary fibrils, and the fixation of coagulated particles on the fibrils.

Colloidal processes play an important part in the production of synthetic rubber, rubber, and plastics. For example, emulsion polymerization as a result of which synthetic rubbers (synthetic latices) are dispersed is a process which occurs in the colloidal system. Rubber and various plastics usually contain very fine particles of mineral fillers which give them the required properties and therefore they should be regarded as colloidal systems.

The main operation of producing lacquers and paints is the granulation of pigments in the relevant media, making them as much dispersed as possible. The colour and covering ability of lacquers or paints greatly depend on the size of pigment particles.

Many major operations in the pharmaceutical industry are essentially colloidal processes. For example, the preparation of emulsions, creams, and ointments consists in the dispersion of the necessary substances in suitable media. Some medicines are administered in the colloidal form. For example, collargol is a very fine dispersion of a silver preparation. The introduction of a medicine in a colloidal form into an organism, first of all, localizes its action and, secondly, increases the length of its action on the diseased organ because such a substance is eliminated from the tissues of the organism far more slowly than when it is introduced as an ordinary solution.

Auxiliary operations in several types of production are often colloidal processes, e.g., the separation of water from oil at the petroleum refinery, the destruction of emulsions which are formed in the chemical types of production when a liquid product is being washed with water, the preparation of various emulsions in the textile, tanning, and other industries. Water purification and gas stripping are typical colloidal processes. Water purification consists in the coagulation of very fine particles suspended in water by electrolytes or in the adsorption of impurities contained in water. A modern technique of gas stripping consists in giving a sufficiently large electric charge to solid or liquid particles contained in a gas or smoke, and then in depositing charged particles on the oppositely charged electrode. Such a technique of gas stripping is considered in greater detail in Chap. 11.

Here, we have considered the importance of colloidal systems and colloidal processes to man, but have said nothing about the role played in nature and industry by high molecular weight compounds whose solutions possess many colloidal properties. The importance of high molecular weight compounds in technology will be shown in Chap. 14. We will only indicate now that the organisms of plants and animals consist of solutions and gels of high molecular weight substances. Therefore, biochemistry and medicine

are connected very closely with colloid chemistry. Many technological processes of the food industry are essentially colloidal ones. In the bread baking industry, swelling phenomena are involved in the preparation of dough, and coagulation phenomena, in bread baking. The preparation of margarine, sauces and mayonnaises is an emulsification process. In the dairy industry, the production of sour milk and cheese is a process of coagulation and syneresis (a phenomenon which is the opposite of swelling). The salting and boiling of meat are also concerned with coagulation or, to be more exact, the denaturation of proteins.

2

OPTICAL PROPERTIES OF COLLOIDAL SYSTEMS

The science of the optical properties of colloidal and microheterogeneous systems is one of the main branches of colloid chemistry. The optical properties of a sol are determined by the properties of colloidal particles, and therefore, the size, shape and structure of particles invisible under the ordinary microscope can be established by studying the optical properties of a system.

Ultramicroscopic observations of colloidal systems have made it possible to verify the main molecular-kinetic concepts which were hypothetical for a long time; the study of optical properties has helped to quantitatively interpret such processes as diffusion, Brownian motion, sedimentation, and coagulation. As cosmic dust, mists, clouds, and very fine suspensions of solid particles in sea and river waters are colloidal and microheterogeneous systems, information on the optical properties of these systems is of practical importance to astrophysics, meteorology, and sea optics. Flying a plane and steering a ship in fog, and photographing by means of infra-red rays, are also directly connected with the optics of colloidal systems. This field of science has made considerable headway in recent years owing to the development of aviation, astronautics, and so forth.

Unfortunately, we are unable to consider all the optical properties of colloidal systems in detail in this textbook because this is an extremely difficult problem and the necessary mathematical operations are very intricate. Therefore, this textbook presents only the principal phenomena and patterns observed when a light beam falls on a colloidal system, and attention is mainly given to the application of these regularities to solving practical problems of colloid chemistry.

The following phenomena may be observed when a light beam falls on a disperse system:

(1) passage of light through the system;

(2) refraction of light by particles of the dispersed phase;

(3) reflection of light by particles of the dispersed phase;
(4) light scattering (this phenomenon is manifested in the form of opalescence);
(5) absorption of light by the dispersed phase with the conversion of light energy into thermal energy.

The passage of light is characteristic of transparent systems having a molecular or ionic degree of dispersion: gases, most individual liquids and true solutions, amorphous and crystalline bodies. The refraction and reflection of light are always observed in microheterogeneous systems as the cloudiness of relatively coarse suspensions and emulsions and also smokes seen in both transmitted (direct) and reflected (side) light. Colloidal systems are mainly characterized by the scattering (diffraction) and absorption of light. Only these two phenomena are considered further because the first three phenomena are the subject of physics textbooks.

1. LIGHT SCATTERING

Attention was drawn to opalescence resulting from light scattering first by Faraday (1857), and then by Tyndall (1869) who observed the formation of a glowing cone when a light beam was passed through a colloidal solution.

Light is scattered only when a light wavelength is greater than the size of a particle of the dispersed phase. If the light wavelength is far smaller than the particle diameter, light is reflected, and this is expressed in turbidity which is noticeable visually. A distinction should be made between the light scattering by particles which conduct electric current and that by particles which do not. Let us first consider the second, simpler case.

Scattered light spreads in all directions, its intensity differing according to direction. If the particles are very small in comparison with the wavelength, light is scattered to the greatest extent at angles of 0° and 180° to the ray incident on a particle. If the particles are comparatively large (but still smaller than the light wavelength), the greatest amount of light is scattered in the direction of the incident ray (forward). Scattered light is usually polarized. For small particles, light scattered at angles of 0° and 180° is not polarized at all, while light scattered at an angle of 90° is completely polarized; for large particles, maximum polarization is observed at an angle which differs from 90°.

It is convenient to represent light scattering in the form of a vector diagram proposed by G. Mie. To obtain such a diagram, the intensity of non-polarized and polarized light expressed in certain units is plotted in the form of radii-vectors in all directions from the point representing a particle, and the terminals of the vectors are

connected by a continuous line. Mie's diagrams for light scattering by a very small particle and a comparatively large one are given in Fig. 2.1 (the arrow shows the direction of light incident on the particle). The external curves on the diagrams connect the terminals of radii-vectors which correspond to the total intensity of scattered light; the internal curves limit the segments of vectors which correspond to the intensity of non-polarized light. Hence, the external,

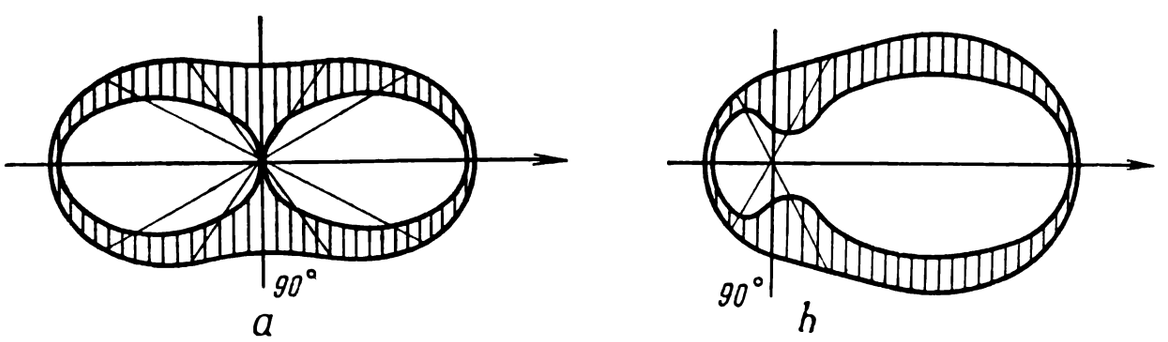

Fig. 2.1. Mie's diagram characterizing the scattering and polarization of light of a very small particle (*a*) and a large particle (*b*)

shaded part of the diagram represents the polarized part of scattered light while the internal part of the diagram represents the non-polarized part of light. The given diagrams relate to light scattering by spherical particles. Later, R. Gans thoroughly studied light scattering by non-spherical particles.

For spherical particles which do not conduct electric current, are small in comparison with the wavelength of the incident light, and are separated by a rather large distance from one another (dilute system), Rayleigh derived the following equation which connects I_0, the intensity of incident light, with I_s, the intensity of light scattered per unit volume of a system:

$$I_s = 24\pi^3 \left(\frac{n_1^2 - n_0^2}{n_1^2 + 2n_0^2} \right) \frac{\nu v^2}{\lambda^4} I_0 \qquad (2.1)$$

where n_1 and n_0 = indices of refraction of the dispersed phase and the dispersion medium;
ν = numerical concentration*;
v = volume of one particle;
λ = light wavelength.

Rayleigh's equation is valid for particles whose size is not more than 0.1 of the light wavelength, or 40-70 nm. For larger particles, I_s changes in inverse proportion not to the fourth, but to a smaller power of λ. Of course, this increases light scattering. W. Heller

* The number of particles contained in 1 cc of a colloidal system is known as "partial" or "numerical" concentration. However, owing to the ambiguity of the first term ("partial" as opposed to "complete"), we will use the term "numerical" concentration.

thoroughly studied the dependence of the exponent at λ on the particle size, mainly with monodispersed lattices of polystyrene whose particle size was determined by means of electron microscopy. In his works (1946), Heller constructed a calibration curve in the coordinates of the particle radius and the exponent at λ. For sols of various polymers, the exponent diminishes from 4 to 2.8.

When the size of particles becomes considerably greater than λ, light is no more scattered but reflected, regardless of the light wavelength. If particles are too large, light reflection from them increases, and this reduces the intensity of scattered light. At the same time, as we see from Rayleigh's equation, the intensity of light scattering also diminishes as the particle size decreases. Therefore, colloidal systems scatter light to the greatest extent.

The following conclusions can be drawn from Rayleigh's equation:

1. For particles of a given size, the intensity of scattered light is directly proportional to the sol concentration. This principle can be used to determine the concentration of the dispersed phase by measuring the light scattering of a sol. However, since multiple scattering occurs at very high concentrations, corrections should be made in Rayleigh's equation.

2. The intensity of scattered light is proportional to the square of the particle volume or, for spherical particles, to the sixth power of their radius. In the Rayleigh region, a decrease of the particle size, the gravimetric concentration of a sol remaining unchanged, causes a corresponding diminution of light scattering.

Rayleigh's equation can be represented as

$$I_s = k\nu v^2 I_0$$

Suppose the particle volume diminishes by x times as a result of disintegration while the gravimetric concentration of the dispersed phase remains unchanged. Then, the numerical concentration will increase by x times, and we will have

$$I'_s = kx\nu\,(v/x)^2 I_0 = (k\nu v^2/x)\, I_0$$

i.e., light scattering will diminish also by x times. This completely coincides with the experimental results which show that the higher the dispersion of a sol, the less does it scatter light. At the molecular degree of disintegration, opalescence cannot be observed.

When the size of particles is considerably larger than the light wavelength, light is not scattered, as we have seen, but reflected; the intensity of scattered light diminishes as the particles grow in size. Fig. 2.2 shows the light scattering of the barium sulphate suspension as a function of the dispersion of a system (at constant gravimetric concentration) expressed in conventional units. Light scattering is characterized by the initial, ascending part of the curve.

Since maximum light scattering corresponds to the colloidal extent of dispersion of a system, the observation of opalescence is among the extremely sensitive methods of detecting the colloidal nature of a system.

3. In opalescence under the action of white light with side illumination, colourless colloidal systems exhibit a dark bluish colour. Since the quantity I_s is inversely proportional to λ^4, dark blue (short) waves are the ones mainly scattered. Conversely, these colloidal systems have a reddish colour in transmitted light because the rays of dark blue light go out of the spectrum as a result of scattering when they pass through the colloidal solution. If the system is illuminated by monochromatic light, this phenomenon is naturally not observed since in this case scattered light can contain only the same wave as that of incident light.

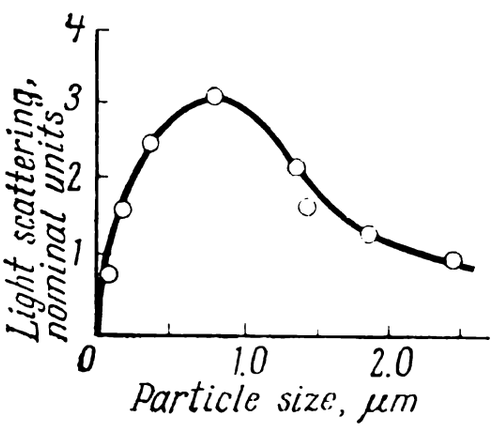

Fig. 2.2. Light scattering by a suspension of barium sulphate as a function of its particle size

The greatest scattering of light having a small wavelength explains the colour of the sky at different times of the day, and also the colour of sea water. The sky is blue in the daytime because the short waves of solar light are scattered by the Earth's atmosphere. The absolute value of the intensity of light scattered by 1 cc of air or water is negligible but it becomes noticeable because of the enormous thickness of the atmosphere and the fluctuation of gas molecules' concentration. The sky is orange or red at sunrise or sunset because mainly light which has passed through the atmosphere is observed in the morning or evening.

The use of dark blue light for blackout, and red light for signalling, is also based on the dependence of light scattering on the light wavelength. Lamps of dark blue light are employed so that they would not be seen from a plane because dark blue rays completely scatter as they pass through a sufficiently thick layer of air, especially if it contains particles of dust or mist. Conversely, lanterns having a red light are used when light must not be scattered and must be noticed in a fog.

4. Opalescence of sols (especially metallic ones) is more intensive than that of solutions of high molecular weight compounds owing to the greater density and, consequently, the higher refraction index of the dispersed phase of the former systems. It is very convenient to observe the effect of the relationship between refraction indices of the dispersed phase and of the dispersion medium on light scattering and turbidity of disperse systems by taking emulsions as an

example. Emulsions are usually very cloudy. However, emulsions of glycerol in carbon tetrachloride stabilized with sodium oleate are transparent because the refraction indices of glycerol and carbon tetrachloride are almost the same and, consequently, the factor in Rayleigh's equation which includes refraction coefficients is practically equal to zero, i.e., the emulsion of glycerol in carbon tetrachloride for all practical purposes does not scatter light.

5. Opalescence of true solutions is very slight because the expression νv^2 in the numerator of Rayleigh's equation is very small owing to the low volume of particles (molecules). However, light scattering may be observed in these cases by using rays of a short wavelength, e.g., X-rays (whose wavelength is 0.04-0.6 nm).

It would seem that individual liquids and gases, about whose coefficients of refraction of the dispersed phase and the dispersion medium is senseless to speak, should not scatter light. However, they do so owing to density fluctuation: the number of molecules as a result of their thermal motion may randomly increase for a very short time in one microvolume of a system and decrease in another microvolume; this leads to a difference in the densities of the substance in microvolumes and, consequently, to a difference in refraction indices.

Besides density fluctuations, solutions undergo concentration fluctuations which may naturally also be a cause of light scattering. Particles of the dispersed phase of colloidal systems may also be formally regarded as concentration fluctuations existing for an indefinitely long time. Because of this, a single approach may be made to the explanation of light scattering by individual liquids, true solutions, and colloidal systems, and Rayleigh's equation may be used in all these cases. We will return to fluctuations in the next chapter.

The foregoing relates to light scattering by colourless colloidal particles which do not conduct electric current. In the specific absorption of some rays, the dependence of the intensity of light scattering on λ^4 and v^2, according to Rayleigh's equation, is upset, the degree of polarization of scattered light changes, and so forth. In a particle which conducts electricity, the electromagnetic field of the light wave induces the electromotive force. As a result, alternating electric current originates in the conductor, just as in the electromagnetic field. Consequently, electric energy is transformed into thermal energy. Under such conditions, short electromagnetic waves (100-1000 nm) are absorbed almost completely. This property of conductors which include metals is the cause of their opacity.

Light scattering by metallic spherical particles has been studied in detail by Mie and Gans. Experiments have shown that when particles conducting an electric current are illuminated, the intensity of opalescence does not grow as the light wavelength diminishes,

but passes through the maximum characteristic of every metal. In addition, the maximum shifts towards long (red) wavelengths when the degree of dispersion decreases, and towards short (blue) wavelengths when it increases. Experiments have also revealed individual opalescence features of sols of many metals.

In conclusion, it should be noted that fluorescence characteristic of true solutions of some dyes, e.g., fluorescein and eosin, is similar in appearance to opalescence. It consists in the fact that the colour of a solution in reflected light differs from that in transmitted light, and the same Tyndall cone as that in typical colloidal systems may be seen. However, they are essentially quite different phenomena. Opalescence originates as a result of light scattering; in this case, the wavelength of scattered light is the same as that of incident light. Fluorescence is an intramolecular phenomenon which consists in the selective absorption of a light quantum by a molecule of a substance and in emission of light of another, longer wavelength. Opalescence is excited by any light while fluorescence is caused by the light of a definite wavelength which is characteristic of a given fluorescing substance.

2. LIGHT ABSORPTION

In 1760, J. Lambert, and still earlier P. Bougeur, in studying light scattering, established the following relationship between the intensity of transmitted light and the thickness of the medium through which it was transmitted:

$$I_t = I_0 e^{-kl} \tag{2.2}$$

where I_t = intensity of transmitted light;
I_0 = intensity of incident light;
k = absorption coefficient;
l = thickness of the absorbing layer.

According to the Bougeur-Lambert law, if the layer thickness of a medium grows arithmetically, the intensity of transmitted light decreases geometrically. In other words, absorption in all the layers into which a given medium can be divided arbitrarily occurs in such a way that every subsequent layer absorbs the same fraction of transmitted light as the preceding one.

A. Beer showed that the absorption coefficient of solutions with an absolutely colourless and transparent solvent is proportional to the molar concentration c of the solute

$$k = \varepsilon c$$

Introducing the value of the molar coefficient of absorption ε into the Bougeur-Lambert equation, we obtain the Bougeur-Lambert-

Beer law

$$I_t = I_0 e^{-\varepsilon c l} \tag{2.3}$$

which establishes the dependence of the intensity of transmitted light on the layer thickness and concentration of the solute. Taking the logarithm of Eq. (2.3), we obtain

$$\ln (I_0/I_t) = \varepsilon c l \tag{2.4}$$

The left member of this equation is known as the *optical density D* of a solution or *extinction.*

In working with monochromatic light, it is always necessary to indicate the wavelength λ at which optical density was determined and to denote this density by D_λ.

The expression I_t/I_0 is known as the *light transmission* or *relative transparency* of a solution.

The left member of the expression

$$\frac{I_0 - I_t}{I_0} = 1 - e^{-\varepsilon c l}$$

is usually known as the *relative absorption* of a solution.

The molar coefficient of absorption which is a constant that is characteristic of a given substance may easily be determined if $c = 1$ and $l = 1$. Then

$$\varepsilon = \ln \frac{I_0}{I_t} \tag{2.5}$$

If $\varepsilon = 0$, the solution does not absorb light, and therefore the Bougeur-Lambert-Beer equation will assume the form

$$I_t = I_0 \tag{2.6}$$

i.e., the intensity of transmitted light will be equal to that of incident light.

The molar absorption coefficient ε depends on the wavelength of the light being absorbed, temperature, and the nature of the solute and the solvent. As a rule, ε does not depend on the concentration of a solution but there may be exceptions when ε changes as the solution is diluted. This is due to a change in the chemical properties of a system, i.e., hydrolysis, hydration, or association. Of course, all this may affect the absorption coefficient ε.

Many attempts have been made to apply the Bougeur-Lambert-Beer law derived for homogeneous systems to colloidal solutions. Experiments have shown that it is quite applicable to sols having a high extent of dispersion if the liquid layer is not too thick and the concentration of a solution is not very high. The application of this law to comparatively low dispersed, greatly opalescing sols is a more difficult matter.

The size of particles of a dispersed phase is not included in the Bougeur-Lambert-Beer equation, and therefore it would seem at first sight that the extent of dispersion of a sol should not affect its ability to absorb light. However, the size of colloidal particles affects light absorption indirectly through light scattering. The fact is that, as a result of light scattering, the white light which passes through loses some radiation (mainly short wavelength radiation), and this can be mistaken for absorption. Unlike the true absorption of light when light energy is absorbed by a system and is transformed into thermal energy, such absorption caused by light scattering is known as *imaginary absorption*.

In this case, Eq. (2.3) will assume the form

$$I_t = I_0 \exp [-(\varepsilon + K')\, cl] \tag{2.7}$$

where K' = coefficient of imaginary absorption caused by light scattering.

Since light scattering depends on the particle size, then

$$K = f(r)$$

where r = particle radius.

If $\varepsilon = 0$, i.e., the sol is white, Eq. (2.7) with imaginary absorption taken into account will assume the form

$$I_t = I_0 \exp(-K'cl) = I_0 \exp(-K''cl/\lambda^4) \tag{2.8}$$

because, according to Rayleigh, light scattering is inversely proportional to λ^4. In imaginary absorption, a sol will naturally be orange in transmitted light and bluish in scattered light. In both cases, the colour is of course not the colour proper of a sol substance but is caused by light scattering.

An experimental verification of Eq. (2.8) has confirmed its validity. The investigation of the dependence of imaginary absorption on the degree of sol dispersion has shown that, as the particle size increases, general absorption at first grows and then begins to diminish after reaching the maximum.

Metallic sols in respect to light absorption and light scattering exhibit anomalous behaviour in comparison with other colloidal solutions. Like light scattering, absorption by metallic sols reaches the maximum at definite values of the wavelength and the particle radius. Fig. 2.3 shows the dependence of light absorption by gold sols on the wavelength of incident light and on the degree of sol dispersion. As we see, when the degree of sol dispersion increases, the maximum on the light absorption curve shifts towards short wavelengths, and the value of this maximum at first grows and then diminishes.

The maximum exists on the light absorption curve owing partially to imaginary absorption, i.e., to light scattering which is the maxi-

mum for metallic sols at an intermediate degree of dispersion. However, light scattering alone is insufficient to cause such an effect. Light absorption grows sharply with an increase in the degree of dispersion also owing to the great ability of metals to absorb light. As a result, even very thin metal layers whose thickness is less than the light wavelength do not transmit light. Of course, at the same concentration of the dispersed phase, sols of metals of higher degree of dispersion will screen light better.

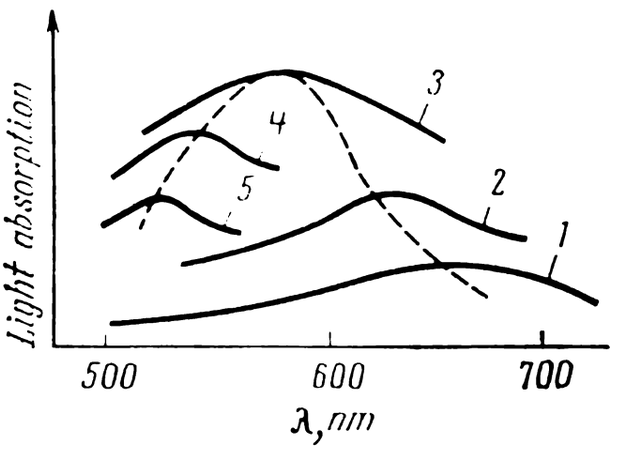

Fig. 2.3. Dependence of light absorption by gold sols on the light wavelength and the extent of sol dispersion (which increases in the order of the growth of the curve number)

The foregoing becomes clear from diagrams I and II in Fig. 2.4. Diagram I shows the transmission of light through a non-metallic sol. In this case, it does not matter whether the dispersed phase exists as coarse or fine particles in a sol: because of its transparency, light

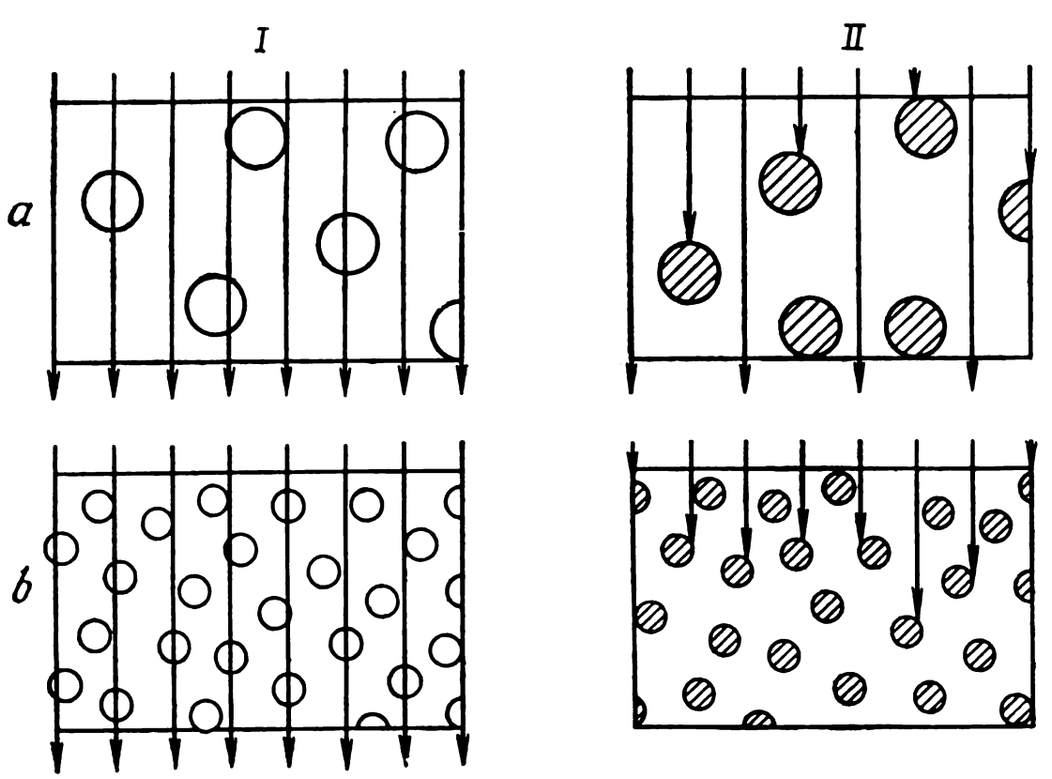

Fig. 2.4. Diagram explaining the change in screening with an increase in the degree of dispersion of non-metallic (I) and metallic (II) sols:
a—coarsely dispersed sols; *b*—highly dispersed sols having the same content of the dispersed phase

passes through both types of particles. Diagram II shows the transmission of light through a metallic sol. Since even very fine

metallic particles possess great ability to absorb light, and the degree of screening rises with an increase in the degree of dispersion, quenching of light, or extinction, will grow as the degree of dispersion of this sol increases. Of course, Fig. 2.4 is only a rough approximation to real situation because it does not take account of the screening of light owing to its scattering which depends on the size of particles of the dispersed phase.

Hence, for metallic sols, the equation for light absorption should take into account the degree of dispersion of a system

$$I_t = I_0 \exp\left[-\varepsilon cl/f\,(r^3)\right] \tag{2.9}$$

As the degree of dispersion grows further, the particles of a metallic sol become so fine that they no longer hinder the passage of light, and in this case sols act as true solutions.

3. COLOUR OF COLLOIDAL SYSTEMS

Colloidal systems are often coloured. The colour of precious or semiprecious stones is determined by the presence of negligible amounts of heavy metals and their oxides in a state of a colloidal extent of disintegration. For example, in natural rubies, such admixtures are iron compounds, and in emeralds, chromium compounds. What is called ruby glass, prepared back in the 18th century by M. Lomonosov, is glass with a very small admixture of colloidal gold (0.0001 per cent). Coloured colloidal systems with a liquid dispersion medium are also found very often. Metallic sols have especially bright colour, owing to the great difference in densities and, consequently, in the refraction indices of the dispersed phase and the dispersion medium.

In general, the colour of sols may be very intensive, even more so than the colour of molecular solutions. For example, when the content of the dispersed phase is the same, the colour of the gold sol is 400 times more intensive than that of the fuchsin solution. The intense colour of colloidal solutions makes it possible to determine negligible amounts of the dispersed phase of a colloid. For example, the yellow colour of the colloidal solution of arsenic sulphide may be detected visually when the layer thickness of a sol is 1 cm; this corresponds to a content of one part of As_2S_3 in 8×10^5 parts of water. The red colour of the gold sol is noticeable under such conditions when one part of gold is contained in as much as 1×10^8 parts of water. This circumstance is widely used in analytical chemistry.

There are many factors that determine the colour of a colloidal system. This colour is affected not only by the nature of the dispersed

phase and the dispersion medium, but also by the degree of dispersion of particles, their shape and structure, because these factors affect the scattering and absorption of light. The colour of a colloidal system may also depend on the technique of preparing a sol and on the conditions of its observation (in transmitted or reflected light). Therefore, only the most general considerations which should be taken into account when dealing with the causes of a sol colour are given below.

Colourless (white) non-metallic sols which do not exhibit selective light absorption usually reveal an orange colour in transmitted light, and bluish opalescence in reflected light. As we have already seen, this phenomenon is caused by light scattering and completely obeys Rayleigh's law.

However, there are many sols with non-metallic particles which have a specific colour that depends on the selective absorption of light rays by their particles. They include the Berlin blue sol which is dark blue, the red sol of antimony sulphide and others. However, as the degree of dispersion diminishes, as in coagulation, the intensity of the sol colour decreases owing to the rapid increase in light scattering. In fact, noticeable changes in the sol colour occur in coagulation only when particles are in close proximity to one another.

The problem of colour of sols containing metallic particles is the most difficult. The colour of metallic sols is determined by the true absorption of light by metallic particles as a result of which some light energy becomes thermal energy; however, this colour is affected also by light scattering. Sols of the same metal may have a different colour because light absorption and scattering pass through a maximum as the particle size and light wavelength increase. For example, coarsely dispersed gold sols are characterized by comparatively low true absorption that is shifted to the red spectral region, and strongly scatter light with the maximum in the same spectral region; these sols usually have a blue colour in transmitted light and red opalescence in scattered light. Conversely, highly dispersed gold sols have usually red colour and blue opalescence owing to their strong ability to absorb light with a sharp maximum in the yellow-green region of the spectrum. At a still greater degree of dispersion, gold sols become yellow and similar in colour to the tolutions of gold chloride, i.e., to molecularly dispersed systems.

The problem of colour of metallic sols in many cases becomes even more difficult, because the shape and structure of particles, in addition to the degree of the dispersion of a system, affect the absorption and scattering of light. The connection between these factors and the colour of metallic sols was analyzed by Mie and Gans.

4. OPTICAL METHODS OF INVESTIGATING COLLOIDAL SYSTEMS

At present, optical methods are most commonly used for determining the size, shape, and structure of colloidal particles, because these methods are rapid and convenient, and the results are precise. Coarsely dispersed systems (suspensions, emulsions, foams, dust) are usually studied by an optical microscope. Highly dispersed colloidal systems are investigated by ultramicroscopy, electron microscopy, nephelometry, and turbidimetry. Flow birefringence, X-ray analysis, and electron micrography are used more rarely for studying the inner structure and the outer surface of particles of a colloidal system.

Only the principles underlying some of these methods are briefly expounded below. The design of the appropriate devices and the techniques of making determinations will not be considered here because the student will understand them fully only by attending practical lessons on colloid chemistry.

Ultramicroscopy. This was one of the first optical methods of studying colloidal systems. Lomonosov described his observation with a microscope of particles suspended in air against a dark background, by focussing light incident on them from the side. However, it was only in 1903 that Siedentopf and Zsigmondy proposed the ultramicroscope, an instrument based on this phenomenon, for studying lyosols. This invention made it possible to confirm the existence of colloidal particles, and thus initiated the rapid development of colloid chemistry.

Theory shows that the resolving power of a microscope, i.e., the smallest distance at which two points may still be seen apart from each other, is about one-half of the light wavelength. Hence, when ordinary light (its wavelength is 400-700 nm) is used, particles whose size is not less than 0.2 μm are resolved by the best microscope. When ultraviolet light is used, smaller particles whose diameter is nevertheless not smaller than 0.1 μm may be discerned by photographing them. Therefore, colloidal particles cannot be seen under the ordinary microscope.

The ultramicroscope makes it possible to ascertain the presence of colloidal particles, to count them and observe their motion. The principle on which the ultramicroscope is based consists in directing a strong beam of light on a colloidal system from the side and observing light scattered by particles with an ordinary microscope. In essence, the principle of the ultramicroscope consists in the observation of the Tyndall cone under the microscope.

The difference in the design of the slit ultramicroscope from that of an ordinary one is easily seen in Fig. 2.5. In an ordinary micro-

scope, observation is made in transmitted light: the particles appear to be dark because they absorb light while the field itself seems to be bright. Conversely, when an observation is made under the ultramicroscope, the field of vision is dark because rays from the light source do not get into the observer's eye, while colloidal particles

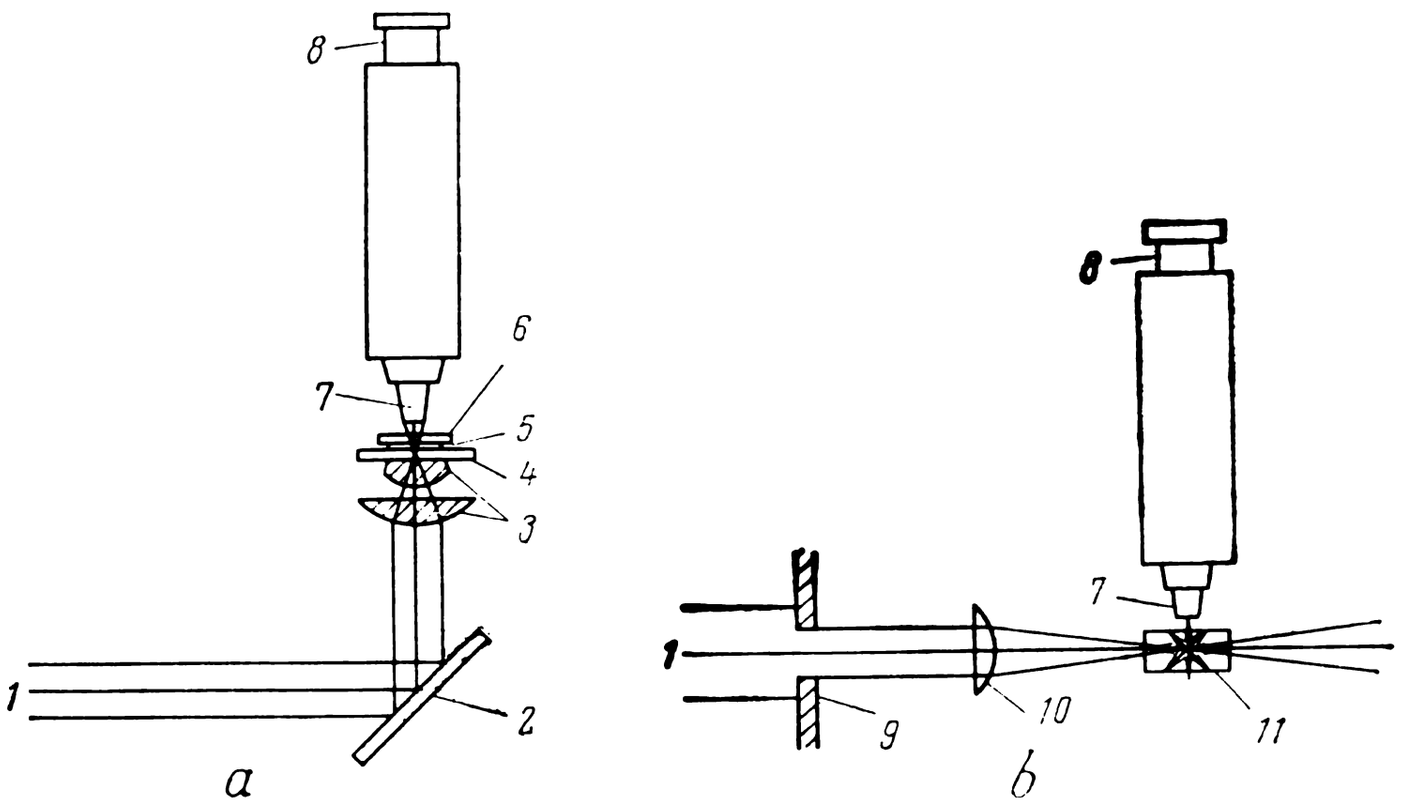

Fig. 2.5. Scheme of the path of rays in the ordinary microscope (*a*) and in the slit ultramicroscope (*b*):

1—light ray; *2*—mirror; *3*—Abbe condenser; *4*—slide; *5*—preparation being examined; *6*—cover glass; *7*—objective lens; *8*—eyepiece; *9*—slit diaphragm; *10*—focus lens; *11*—cuvette containing the sol being examined

seem to be bright as they scatter light. In this case, since the size of colloidal particles is usually smaller than one-half of the light wavelength, they look like luminous points. Particles of freely dispersed systems which are capable of Brownian motion are seen as points which are always in more or less animated motion.

In ultramicroscopic observations, the following conditions must be met:

1. A sol must be sufficiently diluted so that the distance between particles is greater than the resolving power of a microscope. Otherwise, particles will merge and it will be difficult to observe them.

2. Particles should not be too small or too large. In the former case, they may not be seen because of the low intensity of light which they scatter. In the latter, diffraction rings which are formed around large particles will hinder observation.

3. The refraction index of the dispersed phase should greatly differ from that of the dispersion medium. Otherwise, light scattering is small and particles are hardly noticeable.

The ultramicroscope may be used to observe particles whose size is not less than 0.002-0.005 μm in metallic sols. In non-metallic sols, the ultramicroscope may be used to see particles having a diameter of not less than 0.2 μm owing to the smaller difference in the

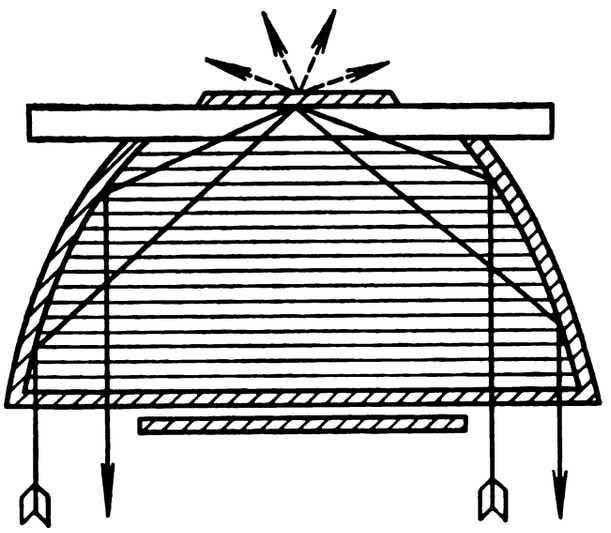

Fig. 2.6. Diagram of the path of rays in a dark-field condenser

refraction indices of the dispersed phase and the dispersion medium. This limit should be even higher for sols having an organic dispersed phase.

Instead of slit ultramicroscopes, dark-field condensers are now widely used to study colloidal systems. These condensers consist of a lens whose top is truncated and whose side surface is silver-plated; they focus light that passes through them on a point which is situated in the field of vision of the microscope and which is, at the same time, in a glass cuvette containing the test system and placed on top of the condenser lens. A round opaque screen fixed in front of the lens prevents direct rays from entering the eyepiece like in the slit ultramicroscope, only the rays scattered by colloidal particles get in. The path of rays in the dark-field condenser is illustrated in Fig. 2.6. This condenser is very simple and can be adapted to any ordinary microscope.

The ultramicroscope (or a microscope with the dark-field condenser) cannot be used to directly determine the size of colloidal particles; however, this can be done indirectly. A volume in the form of a rectangular parallelepiped is optically isolated in a preparation of the test sol by one method or another, and the number of colloidal particles in the parallelepiped is counted.

If the height of the parallelepiped is denoted by h, and the side of the square which is the rectangular parallelepiped base, by l, the volume in which particles are counted will be $V = hl^2$. Since

colloidal particles are usually in animated Brownian motion and their quantity in the chosen volume always changes, it is necessary to take the average value of the numerous counts made at definite time intervals. The volume in which the quantity of particles is counted, and the numerical concentration should not be too large so that the observer can immediately determine the number of particles in a volume.

After calculating the average number of particles n in an isolated volume V, it is easy to find the numerical concentration ν:

$$\nu = n/V \tag{2.10}$$

If ρ, the density of the dispersed phase, and c, the weight concentration of a sol, are known, then

$$v\rho\nu = c \tag{2.11}$$

where v = average particle volume.

Whence

$$v = c/\rho\nu \tag{2.12}$$

If the particle is spherical, its radius may be easily found by the equation

$$r = \sqrt[3]{3v/4\pi} \tag{2.13}$$

If the particle is cubic, the size of its edge is calculated by the equation

$$l = \sqrt[3]{v} \tag{2.14}$$

By observing colloidal systems under the ultramicroscope, it is possible not only to determine the average particle size, but also to get some idea of the particle shape. If the particles seen in the dark field glimmer, this indicates their anisodiametric nature. They glimmer, because non-spherical particles which are in Brownian motion turn to the light ray by their diverse planes that are unequal in area, thus sending a different amount of light at different times to the observer's eye. If the particles in the dark field glisten with a soft, non-glimmering light, this indicates their approximately isodiametric form.

A shortcoming of determining the particle size by means of the ultramicroscope is that the value found corresponds to the average particle size. In addition, such a determination is very tiresome (for the results to be sufficiently reliable, it is necessary to take the average of hundreds and even thousands of separate determinations).

B. Deryagin and G. Vlasenko constructed a special flow ultramicroscope by means of which the number of particles per unit volume of an aerosol or lyosol may be determined very rapidly. The design

of this microscope is illustrated in Fig. 2.7. The lyosol or aerosol under consideration is observed in a flow directed along the channel of cuvette *2*, which is parallel to the axis of the microscope tube *5*. Every particle flashes as it crosses the zone illuminated with the light source *3*; the total number of such flashes can be easily counted.

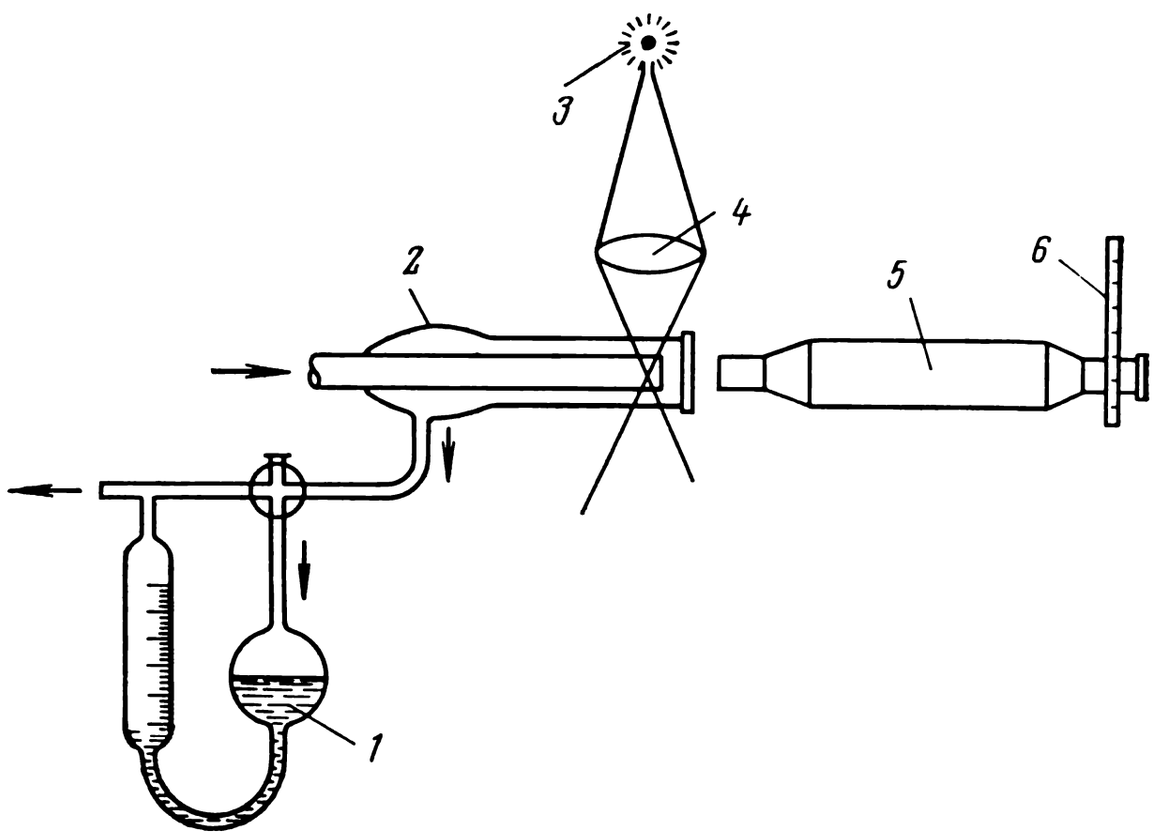

Fig. 2.7. Scheme of the flow ultramicroscope:
1—volume meter; *2*—cuvette; *3*—light source; *4*—lens; *5*—microscope tube; *6*—eyepiece diaphragm

The numerical concentration may be easily found by dividing the number of counted flashes by the total volume (measured by meter *1*) of the aerosol that flows through the part of the field which is under control and cut out by the eyepiece diaphragm *6*.

Such a method of determining the numerical concentration eliminates almost all the sources of errors which may be made by the classical ultramicroscopic counting method; in addition, far less time is required for an investigation. For example, when the flow method is used to determine very small concentrations of aerosol remaining after suction through aerosol filters, measurement time is reduced by a hundred times and even more with a simultaneous increase in the precision of determination.

In the flow ultramicroscopic counting method, particles may be counted automatically and, by dividing them into fractions or classes according to brilliance, the particles of every fraction can be counted, i.e., the fractional composition of the dispersed phase

can be studied. When particles are counted automatically, light falls on the photomultiplier cathode. Every flash caused by a particle that passes through the cuvette induces an electric pulse which is ergistered by a meter after intensification.

The flow ultramicroscope is now widely used in several research institutions, shafts and by expeditions in the Soviet Union.

Electron microscopy. In the electron microscope, a beam of fast electrons is used instead of light rays; this sharply increases the resolving power of the microscope and makes it possible to directly see or photograph colloidal particles. Electrons can be used in this case because they have a quantum nature and at the same time a wave nature. The wavelength of the electron flow is only 0.02-0.05 Å, i.e., it is smaller than an atom, and the resolving power therefore may be brought to 5-10 Å by the electron microscope. The image obtained on the fluorescing screen may be photographed and the photograph magnified; thus the total magnification by modern electron microscopes is very great.

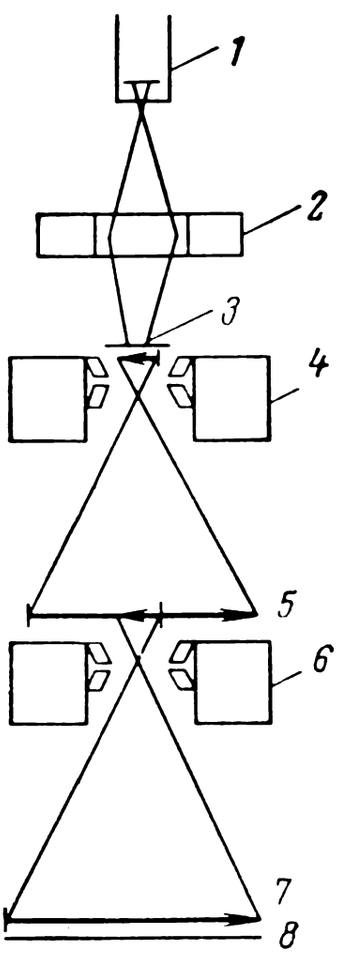

Fig. 2.8. Diagram of the path of rays in the electron microscope:
1—source of fast electrons (electron gun); *2*—condenser lens; *3*—object being examined; *4*—objective lens; *5*—intermediate image; *6*—projection lens; *7*—final image on the fluorescent screen; *8*—photographic plate

The path of the electron beam in the electron microscope is illustrated in Fig. 2.8. In general, it is similar to the path of light in the ordinary microscope. However, since electrons are readily scattered and absorbed, electromagnetic coils which create electrostatic or magnetic fields are used for focussing the electron beam. A high vacuum is maintained in the electron microscope in order to reduce electron scattering. For the same purpose, we use objects of a very small thickness that are deposited usually on a very thin nitrocellulose, quartz, carbon, or other film which is transparent for the electron beam. If the last condition is not met, the object may become heated and destroyed under the action of electrons. Instead of the objects, their imprints on films (*replicas*) are often examined under the electron microscope. Such replicas are made more contrast by

shadowing them with a molecularly disintegrated metal (e.g., chromium).

A shortcoming of electron microscopy is the difficulty of preparing test objects and the need for maintaining a high vacuum in the microscope. In addition, since the object is studied in a vacuum, not the colloidal system as such, but only particles contained in its dry residue, can be seen under the electron microscope. However, the electron microscope is being used on an ever wider scale in science and technology because the shape and structure of very fine particles can be seen with it. Even large molecules (proteins, nucleic acids) and viruses can be watched owing to its high resolving power.

Fig. 2.9 shows photographs made by means of the electron microscope.

Nephelometry. The technique is based on the ability of colloidal systems to scatter light. By determining the intensity of light scattering by a system, it is possible to determine the size of particles or the concentration of the dispersed phase, to study coagulation phenomena, and so forth. Nephelometry is widely used in colloid chemistry because it is a highly sensitive, and also simple, method.

Nephelometry is based on the relation expressed by Rayleigh's equation

$$I_s = k\nu v^2 I_0 = k\nu v \cdot v I_0 = kcvI_0 \qquad (2.15)$$

where c = volumetric concentration of the dispersed phase in a system.

The average volume of a particle may be calculated when all the quantities in Rayleigh's equation (2.1) and c, the volumetric concentration of the dispersed phase, are known, and the absolute values of the intensity of incident and scattered light (I_0 and I_s) are determined.

The absolute values of the intensity of incident and scattered light may be found only by means of intricate instruments (Tyndall meters), and several corrections must be made in the results obtained. Moreover, in determining the absolute values of light intensity, monochromatic light must be used. Therefore, relative methods of nephelometry which do not have most of these difficulties are used far more commonly.

In relative measurements, opalescence of the test solution is compared with that of the standard solution whose particle size v'' is known, and the size of particles v' in the system under consideration is calculated by using the data obtained. A prerequisite of such a determination is the same volumetric concentration of the dispersed phase in both solutions.

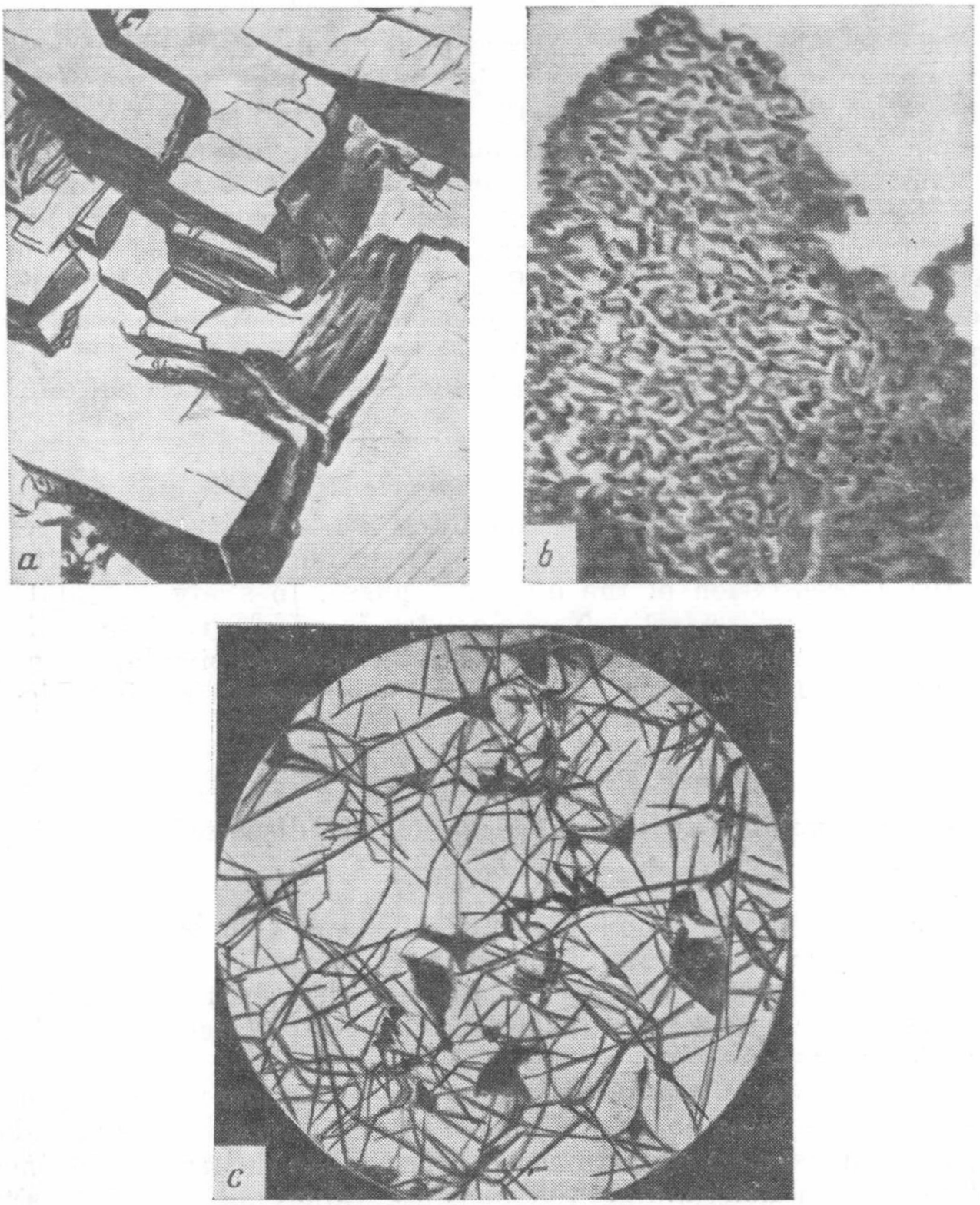

Fig. 2.9. Electron microphotographs:
a—etched surface of aluminium (×6000); *b*—surface of activated charcoal; *c*—particles of zinc oxide (×10,000)

To make measurements by such a technique, very simple devices, i.e., nephelometers, are used. The design of the simplest of such devices, Kleinmann's visual nephelometer, is given in Fig. 2.10. It has two identical glass cylindrical cuvettes *4* and *5*; the standard solution is put into the first cuvette, and the test solution, into the second one. The light from source *1* (which is behind the figure plane) falls uniformly on both cuvettes. The height of the illuminated column of liquid in each cuvette can be controlled by raising and lowering special screens *2* and *3*. The light scattered by solutions falls on solid glass cylinders *6* and *7* which are immersed in solutions to the same depth (these cylinders are used to prevent the reflection of light by the menisci of liquids). From the cylinders, the beams of scattered light are directed by prisms *8* and *9* to eyepiece *10* which is divided in half. Each half is illuminated by the light that enters from one of the cuvettes.

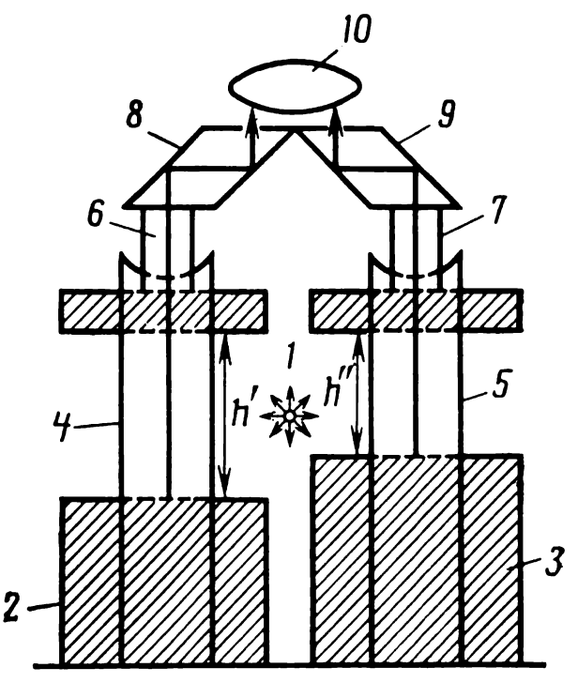

Fig. 2.10. Diagram of Kleinmann's nephelometer:
1—light source; *2*, *3*—mobile screens; *4*, *5*—cylindrical cuvettes; *6*, *7*—glass cylinders; *8*, *9*—prisms; *10*—eyepiece

When working with the nephelometer, the test and standard solutions are poured into the cuvettes, and the same degree of illumination of both halves of the eyepiece is attained by raising or lowering the cuvette screens. Apparently, I'_s, the intensity of light scattered by the test solution, is equal to I''_s, the intensity of light scattered by the standard solution. Then

$$I_0 k v' c h' = I_0 k v'' c h'' \tag{2.16}$$

because the intensity of light scattered by each cuvette is proportional to h, the height of its illuminated part.

It follows from Eq. (2.16) that

$$v'h' = v''h'' \tag{2.17}$$

or

$$v'/v'' = h''/h' \tag{2.18}$$

whence

$$v' = v''\,(h''/h') \tag{2.19}$$

Knowing the size of particles contained in the standard solution, we use Eq. (2.19) to calculate the size of particles of a test sol. Of course, it should be borne in mind that the results of such calculations are reliable only when colloidal systems are monodispersed. In addition, since the exponent of λ in Rayleigh's equation does not depend on the particle size only for highly dispersed sols, the given technique can be used to determine the dimensions of comparatively small particles.

Since light scattering greatly depends on the particle size, the determination of a change in the intensity of opalescence can be successfully used to study the aggregation and disaggregation which occur in a system. To this end, it is expedient to draw graphs, plotting the values of light scattering by a sol on the ordinate, and observation time, on the abscissa.

The nephelometer can also be used to determine the concentration of the dispersed phase in a system, by means of the formula

$$c' = c'' (h''/h') \tag{2.20}$$

whose derivation is similar to that of Eq. (2.19). Of course, the standard and test solutions should contain particles of the same nature and the same size.

Photoelectric nephelometers are used more commonly now. They have sensitive microammeters to determine the intensity of the photoelectric currents i' and i'' which are induced in photoelectric cells by light scattered by standard and test solutions. When photoelectric nephelometers are used, the size of particles and the concentration of the dispersed phase in a sol are determined by the equations

$$v' = v'' (i'/i'') \tag{2.21}$$

and

$$c' = c'' (i'/i'') \tag{2.22}$$

Nephelometry may also be sometimes used to determine the concentration or dimensions of particles of sols which weakly scatter light. In this case, it is necessary to work not in the visible, but ultraviolet, region of the spectrum. Data for calculating the numerical concentration or size of particles can be obtained by using the appropriate light source, quartz lenses, and a device which registers the current of a photoelectric cell.

To determine the particle size, not only the ability of colloidal systems to scatter light is used (nephelometry), but also their ability to weaken the intensity of transmitted light as a result of light scattering (**turbidimetry**). Here, turbidity is measured by ordinary colorimeters or spectrophotometers. Turbidimetry is now widely used in colloid chemistry; this method is described in detail in textbooks of analytical chemistry.

The dimensions (and in some cases, the shape) of colloidal particles may be determined also by using other optical characteristics of a colloidal solution*. However, all these methods are outside the scope of this textbook.

It should be noted that all the methods of determining the size and shape of colloidal particles by measuring light scattering are suitable mainly for colourless (white) sols. For coloured, and especially metallic, sols these methods cannot be used without substantial corrections.

X-Ray analysis and electron micrography. Both of these methods, based on the application of X-rays or the electron flow, are considered in detail in textbooks of physical chemistry, and therefore we will not deal with their underlying principles here. It should only be noted that X-ray analysis supplies information on the internal structure of colloidal particles. Because of their small size, it is difficult to obtain the Laue diagrams, and therefore only the Debye-Scherrer diagrams are obtained and studied in most cases.

The crystalline structure of particles of many sols has been established by studying the Debye-Scherrer diagrams. The best results were obtained for the sols of heavy metals and their compounds because heavy atoms strongly scatter rays, while the dispersion medium here is a comparatively small obstacle to analysis. The structure of the dispersed phase greatly depends on the method of preparing a sol and on its age. Studies by V. Kargin and Z. Berestneva which show that sol aging is, as a rule, connected with the crystallization of the dispersed phase will be considered in Chap. 8.

X-ray analysis is important for studying high molecular weight substances, the structure of natural and synthetic polymers, the nature of swelling, and so forth. An analysis of the Debye-Scherrer diagrams makes it possible in many cases to establish the periodicity of polymer molecules and their three-dimensional structure although all this requires very long and scrupulous calculations with computers. It was precisely the methods of X-ray analysis that have helped establish the complicated molecular structure of penicillin, vitamin B_{12}, hemoglobin, and many other high molecular weight substances.

A modification of the X-ray analysis is the determination of the average particle size by scattering X-rays at small angles. This furnished valuable information on the dimensions of protein molecules and on the extent of their hydration.

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* The investigation of the shape and structure of colloidal particles, based on the determination of flow birefringence, was considered in the first edition of this book, published in Russian, S. S. Voyutsky, *Kurs kolloidnoi khimii*, Moscow, Khimiya, 1964.

Owing to the low permeability of the electron beam, electron micrography makes it possible to thoroughly study only the surface of particles of the dispersed phase of colloidal systems and macromolecules of high molecular weight substances. Electron micrography makes it possible to directly determine the distance between atoms on the surface, and this may be used for finding other parameters of the structure of a substance. This method is especially suitable for studying adsorption layers.

The combination of electron micrography with X-ray analysis supplies sufficient information on the internal structure of the dispersed phase of colloidal systems and solutions of high molecular weight substances, and on changes caused in this structure by heating, deformation, swelling, and other effects.

3

MOLECULAR-KINETIC PROPERTIES OF COLLOIDAL SYSTEMS

1. THERMAL MOTION OF MOLECULES AND BROWNIAN MOTION

According to the molecular-kinetic theory, gas is an aggregate of molecules or atoms which are in chaotic motion. The average intermolecular distance in gases is considerably greater than the linear dimensions of molecules, and the total volume occupied by molecules proper is negligible in comparison with the gas volume. As gas molecules collide with one another, they change the velocity and direction of their motion; but their average kinetic energy which depends only on temperature remains always equal to $^3/_2 kT$ (where k is the Boltzmann constant and T absolute temperature).

Molecules, atoms, or ions in solid crystalline bodies are arranged in a definite order which corresponds to the least value of free energy, and they vibrate near equilibrium positions, i.e., the points of a crystal lattice.

Liquids by their properties hold an intermediate position between gases and solids. By their density, they are similar to solids: the intermolecular distance in a liquid is almost as small as that in crystals, and is similar to the dimensions of molecules. However, molecules of liquids, just as molecules of gases, are capable of changing their places, but without coming out of the sphere of influence of the molecular forces of neighbouring molecules.

It was believed earlier that molecules in a liquid were arranged randomly in respect to one another. However, X-ray analysis has shown that there is a definite order of molecular arrangement in very small regions of a liquid. It is assumed that the structure of a liquid is characterized by a short-range order, unlike crystals having a long-range order. The regions having a quasicrystalline order in a liquid are stable only temporarily: after arising and existing for a very short time, they disintegrate and are formed in another place.

According to the modern theory of liquids proposed independently by Frenkel and Eiring, when molecules move in a liquid and a molecule changes its place, the adjacent molecules are being rearranged

until every molecule again occupies a position which is the most favourable one energetically. Let us consider Ya. Frenkel's concepts in somewhat greater detail.

The presence of a short-range order and the absence of a long-range one in a liquid indicates that its molecular packing has *voids* or *holes*. An elevation of temperature increases the number of holes and decreases quasicrystalline orderliness. The presence of holes is what determines the ability of a liquid to flow and increases its volume on melting.

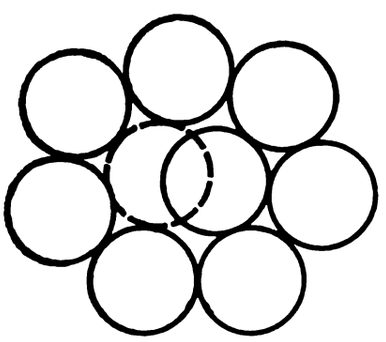

Fig. 3.1. Diagram of the arrangement of molecules near a hole

Many molecules of a liquid may be arranged next to holes, as is represented in Fig. 3.1. Energetically, such molecules are in a potential hole and are separated from other possible equilibrium positions by an energy barrier. However, each of these molecules can overcome the barrier ("to make a jump"), provided it has enough energy, and occupy the adjacent hole, passing over to a new equilibrium position. As a result, a molecule leaves a hole which may be occupied by another molecule. The number of possible "jumps" is the larger, the greater is the number of holes and the lower is the energy barrier which a molecule must overcome to pass from one equilibrium position to another.

Such a jump of molecules apparently determines their thermal motion in a liquid, or *self-diffusion*. As temperature rises, the rate of self-diffusion increases because the molecule arranged next to a hole is very likely to acquire the energy needed for overcoming the energy barrier. Moreover, the rate of diffusion grows with temperature owing to an increase in the number of holes upon the thermal expansion of a liquid. The minimum energy required for a molecule of a liquid to move from one temporary position of equilibrium to another is known as the *activation energy of diffusion*. This quantity depends on the density of packing of molecules, their size, and intermolecular forces

In the above case of self-diffusion, jumps made by molecules are just as frequent in all directions if there is no external force field, and therefore such a process does not cause a transfer of a substance in mainly one direction. In the presence of an external force field, e.g., shear stress, a jump in the direction of the field action is more probable because the activation energy here is less than that required for a jump in the opposite direction. As a result, forced diffusion occurs, causing the viscous flow of a liquid (the latter is considered in Chap. 10).

The diffusion of molecules of a substance dissolved in a liquid is explained similarly. The molecules of a substance in a solution make jumps in almost the same way as the molecules of a solvent. They cannot remain in a definite place owing to their random motion but are distributed on the average uniformly throughout the liquid volume. Thermodynamically, this corresponds to an increase in the entropy of a system.

The thermal motion of every molecule of a liquid consists partially of vibrations near the equilibrium position and partially of small translatory motions when, owing to an especially strong collision with a neighbouring molecule or several random collisions with molecules in similar directions, the molecule moves so far away from the equilibrium position that it is closer to a new equilibrium position. Hence, all molecules of a liquid lead kind of "nomadic life"; besides, short-term movements (jumps from one equilibrium position to another) are replaced by relatively long periods of "settled life" (vibration around the equilibrium position). It is the comparatively long periods of "settled" existence of molecules in liquids that explain why diffusion in liquids occurs far slower than in gases.

At high temperatures, liquids resemble gases by their properties. In the critical state, distinction between a liquid and a gas disappears, and at temperatures higher than critical one, a liquid becomes a gas. Conversely, at low temperatures which are close to crystallization temperatures, liquids resemble crystals by their properties. However, a liquid passes over to a crystalline state always by leaps. When, for some reason, liquids cannot pass over to a crystalline state, they pass over to a glassy (amorphous) state with a drop in temperature.

Thermal motion of particles in colloidal and microheterogeneous systems has become known as *Brownian motion* after the English botanist R. Brown who discovered it in 1827 when he was examining an aqueous suspension of flower pollen under a microscope. Brown could not explain the nature of this phenomenon but he established that the motion of pollen particles does not decrease with time and does not depend on external energy sources (light, shocks), and that it is the more intensive, the higher is the temperature. Later, various scientists tried to explain Brownian motion by the vital activity of pollen, the presence of convection currents in a system, electric phenomena, and the nonuniform wetting of particles by the medium. However, the first assumption had to be discarded because Brownian motion turned out to be characteristic of not only the pollen suspension, but all suspensions in general, including those of inorganic substances. The explanation of Brownian motion by microscopic convection currents in a liquid turned out to be untenable since the neighbouring particles then had to move at the same rate and parallel to one another. In fact, microscopic observation shows

that neighbouring particles move at different rates along paths that cross one another at different angles. Brownian motion can neither be interpreted in terms of electric forces and the non-uniform wetting of the particle surface with the dispersion medium.

Gouy (1888) and Exner (1900) assumed that Brownian motion had a molecular-kinetic nature, i.e., it was the result of thermal motion. The correctness of this viewpoint was confirmed by the theoretical

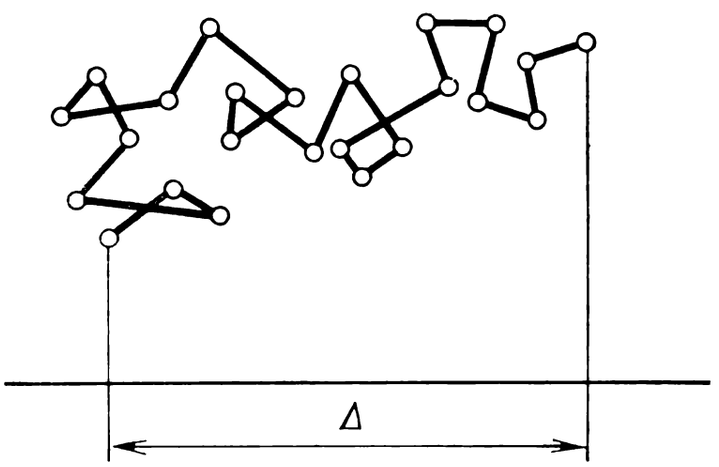

Fig. 3.2. Diagram of Brownian motion of particles

estimations made by Einstein and Smoluchowski, and by experiments performed by Perrin, Svedberg, and several other scientists. It is now definitely established that the motion of colloidal particles is the result of random blows on them by the surrounding molecules which are in thermal motion. If a particle is small enough, the number of blows on it from different sides is usually not the same, and the particle receives intermittent impulses that force it to move in different directions along very complicated paths. As the size and mass of a particle grow, the probability of compensation of blows increases and its inertia becomes greater. Hence, large particles whose size is 5 μm make movements which we perceive as vibrations around a centre. When the diameter of a particle is larger than 5 μm, Brownian motion practically ceases. Besides translatory motion, small particles are also in rotary Brownian motion caused by blows with molecules.

A colloidal particle changes its direction and rate very often as a result of the enormous number of blows on it by the molecules of a medium. In one second, a colloidal particle may change its direction by more than 10^{20} times. Under such conditions, it is impossible to determine the true path of a colloidal particle, but it is easy to determine its average displacement per unit time. Fig. 3.2 illustrates the projection of motion of a particle on a plane. This projection can be found by observing the Brownian motion of a particle under the microscope and registering its position in the field of vision at equal time intervals. In this case, the motion of

a particle from one registered position to another is represented by a straight line only conventionally. In fact, it also has a very complicated zig-zag path in space. Usually, interest is taken in the movement of particles in a definite direction (for example, in the direction of diffusion). Therefore, $\bar{\Delta}$, the root-mean-square value of the projection of displacement of a particle on axis x parallel to the selected direction, is taken instead of displacement, or shift, for quantitative calculations which will be considered below. The arithmetical mean value of the projection of displacement cannot be used because it is equal to zero owing to the equal probability of all directions of motion of a particle. The root-mean-square value of the projection of displacement is found by the equation

$$\bar{\Delta} = \sqrt{\frac{\Delta_1^2 + \Delta_2^2 + \Delta_3^2 + \dots}{n}} \tag{3.1}$$

where Δ_1, Δ_2, Δ_3 . . . = projections of displacements of a particle on axis x;
n = number of such projections taken for calculation.

2. DIFFUSION IN TRUE SOLUTIONS AND IN COLLOIDAL SYSTEMS

Diffusion is the spontaneous equalization of the concentration of molecules, ions, or colloidal particles in a system as a result of their thermal chaotic motion. Hence, diffusion is a macroscopic exhibition of the thermal motion of molecules, and therefore it is the more rapid, the higher is the temperature. Diffusion is irreversible, it occurs until concentrations are completely equalized because the maximum entropy of a system corresponds to the chaotic distribution of particles.

Osmotic pressure is often assumed to be the cause of diffusion. This concept was evolved by Nernst (1885). Since osmotic pressure may be exhibited only in the presence of a semipermeable partition (membrane), it is senseless to regard this pressure as a real force independent of the membrane. Nevertheless, it is sometimes convenient to assume osmotic pressure, which is also the result of the chaotic motion of molecules, to be the cause of diffusion. The correctness of such an approach is confirmed by the conformity of theoretical data obtained on the basis of this viewpoint with experimental evidence.

Regularities of mass transfer by diffusion are formally similar to those of the transfer of heat or electricity. Using this similarity,

Fick (1855) formulated the first law of diffusion

$$dm = -D\frac{dc}{dx}s\,d\tau \tag{3.2}$$

where m = mass of the diffusate;
D = diffusion coefficient which depends on the properties of the diffusing particles and the medium;
dc/dx = concentration gradient;
s = cross-sectional area of diffusion flow;
τ = duration of diffusion.

The negative sign is put before the right-hand member of the equality because the derivative dc/dx has a negative value as the quantity c decreases with an increase in the values of x.

Eq. (3.2) may also be represented as

$$i_d = 1/s\,(dm/d\tau) = -D\,dc/dx \tag{3.3}$$

The quantity i_d is known as the *density of diffusion flow*. It characterizes the amount of a substance transferred by diffusion per unit time through a section equal to unit area.

The diffusion flow generally is a function of c and x because the concentration gradient dc/dx depends on these quantities. Only if the concentration gradient is kept constant, does the diffusion flow remain unchanged in the course of time and is a stationary diffusion process established in a system. For this case, we may apparently write

$$m = -D\frac{dc}{dx}s\tau \tag{3.4}$$

Assuming that $dc/dx = -1$, $s = 1$, and $\tau = 1$, we obtain

$$D = m \tag{3.5}$$

i.e., the diffusion coefficient D is numerically equal to the amount of a substance which has diffused through unit area per unit time when the concentration gradient is unity. It follows from Eq. (3.4) that the diffusion coefficient is measured in units of cm^2/sec. However, when diffusion phenomena are being considered, the day instead of the second is taken very often as unit time because the process is very slow.

Einstein (1908) derived the equation to connect D, the diffusion coefficient, with T, the absolute temperature of a system, η, the viscosity of the dispersion medium, and r, the radius of particles of the dispersed phase. To derive this equation which is of great practical and theoretical importance let us suppose that a tube has a section of s cm^2 and is filled with a solution as is represented in Fig. 3.3. The concentration of the solute uniformly decreases from left to right. In the tube let us imagine a layer of the solution which

is infinitely thin and is limited by the planes x_1x_1' and x_2x_2'; V, the volume of this elementary layer, will be sdx. Let us denote the concentration of the solution and osmotic pressure to the left of this layer by c_1 and π_1, and to the right of it, by c_2 and π_2. Apparently, $c_1 > c_2$ and $\pi_1 > \pi_2$. Under such conditions, the solute diffuses in the tube from left to right as is indicated in the figure by an arrow. Diffusion is caused by the chaotic thermal motion of particles which

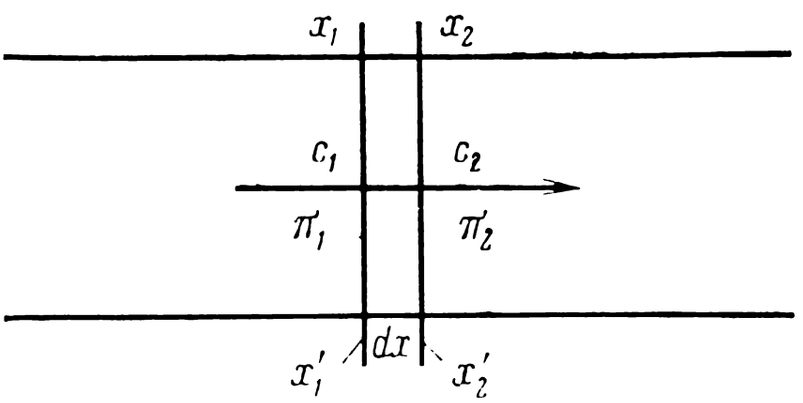

Fig. 3.3. Diagram explaining the derivation of Einstein's equation

move at separate moments at a different rate and in different directions. However, in considering diffusion on the whole as a directed flow of particles, we may speak of some effective constant velocity. Such a velocity must be possessed by all particles, so that they could transfer, moving in a straight line, a definite amount of a substance per unit section and per unit time at a given concentration gradient.

The constant velocity of diffusing particles may be explained only by the fact that the motive force f which acts on a particle is counterbalanced by the reversely directed friction force f' which is experienced by the particle, i.e.,

$$f = f' \tag{3.6}$$

The friction force f' is equal to the product of B, the coefficient of friction between the particle and the medium, by u, the rate of motion of the particle

$$f' = Bu \tag{3.7}$$

According to Stokes' law, the coefficient B for spherical particles is equal to $6\pi\eta r$ (where η is dynamic viscosity of the medium, and r, the radius of the particle).

To calculate the motive force acting on a particle, let us at first determine the motive force F per unit volume of the elementary layer. Apparently,

$$F = \frac{s(\pi_2 - \pi_1)}{s\,dx} = -\frac{\pi_1 - \pi_2}{dx} = -\frac{d\pi}{dx}$$

Then, denoting the molar concentration of a solute in the elementary layer by c, we can represent the motive force f per particle as

$$f = -\frac{d\pi}{c\,dx N_A} = -\frac{RT}{cN_A}\cdot\frac{dc}{dx} \tag{3.8}$$

where R = universal gas constant;
T = absolute temperature;
N_A = Avogadro number.

Substituting the expressions found for f' and f in Eq. (3.6), we obtain

$$Bu = -\frac{RT}{cN_A}\cdot\frac{dc}{dx} \tag{3.9}$$

This equation may be rewritten as

$$uc = -\frac{RT}{N_A}\cdot\frac{dc}{dx}\cdot\frac{1}{B}$$

However, uc is merely m, the amount of a substance that has diffused per unit time through unit area. Therefore

$$m = -\frac{RT}{N_A}\cdot\frac{dc}{dx}\cdot\frac{1}{B} \tag{3.10}$$

According to Fick's equation, for the same conditions

$$m = -D\frac{dc}{dx} \tag{3.11}$$

Equating the right-hand members of Eqs. (3.10) and (3.11) we find

$$D = \frac{RT}{N_A}\cdot\frac{1}{B} = \frac{kT}{B} \tag{3.12}$$

This is precisely Einstein's equation. For particles whose shape is almost spherical, $B = 6\pi\eta r$ and

$$D = \frac{RT}{N_A}\cdot\frac{1}{6\pi\eta r} = \frac{kT}{6\pi\eta r} \tag{3.13}$$

The diffusion coefficient is directly proportional to absolute temperature and inversely proportional to the viscosity of a medium and the particle radius. The diffusion coefficient is small in colloidal systems because the dimensions of colloidal particles are very large in comparison with those of ordinary molecules. Therefore Graham drew the incorrect conclusion that there is no diffusion in colloidal systems.

Using Einstein's equation, we can easily determine the mass of one mole of a substance if the values of D, T and η are known. Indeed, it follows from Eq. (3.13) that

$$r = kT/(6\pi\eta D) \tag{3.14}$$

After determining the particle radius by Eq. (3.14) we can calculate M, the mass of one mole of a substance:

$$M = {}^4/_3\pi r^3 \rho N_A \qquad (3.15)$$

where ρ is the density of the dispersed phase which is usually known.

Hence, the molecular weight of a substance (which is numerically equal to the mass of one mole of the substance) may be determined by measuring the diffusion coefficient.

Proceeding from the determination of the diffusion coefficient in aqueous solutions, Perrin and Herzog calculated the molecular weights of some carbohydrates. They assumed that these molecules were spherical and so small that water could be regarded as a continuum; therefore, the molecular radius and, consequently, the coefficient B did not grow owing to the solvation of the solute. Their results are given in Table 3.1.

Table 3.1. **Molecular Weight of Carbohydrates Calculated from the Diffusion Coefficient**

Carbohydrate	D, cm²/day	ρ, g/cc	M	
			empirical value	theoretical value
Arabinose	0.540	1.6182	120	160
Sucrose	0.384	1.5873	332	342
Lactose	0.377	1.5245	331	342
Maltose	0.373	1.4992	336	342
Raffinose	0.316	1.5017	553	504

Notwithstanding the allowances made, the experimental results coincide quite satisfactorily with the estimated ones on the basis of the data on the chemical structure of these substances.

Many methods have been proposed to experimentally determine the diffusion coefficient. In all of them, the solution of a diffusing substance is added to the solvent so that an interface which is as clear as possible would be formed between them. The system obtained is kept for some time at constant temperature under conditions which completely exclude shaking and thermal convection. Then, the new distribution of concentration of the solute in the system that was attained by diffusion is determined. The diffusion coefficient is calculated according to the results obtained, usually by means of special tables.

Various modifications of this technique differ from one another only by the apparatus used and the way of determining the distribution of concentration of a substance after diffusion. The distribution of concentration may be established by careful sampling and analyz-

ing the samples, and also by determining the change of colour, light absorption, or the refraction index of a solution along the liquid column. The experimental methods of determining the diffusion coefficient are described in detail in manuals of physical and colloid chemistry.

As we have seen, diffusion in true solutions is caused by the thermal motion of molecules. Similarly, the diffusion of the dispersed phase in colloidal systems is caused by the Brownian motion of particles.

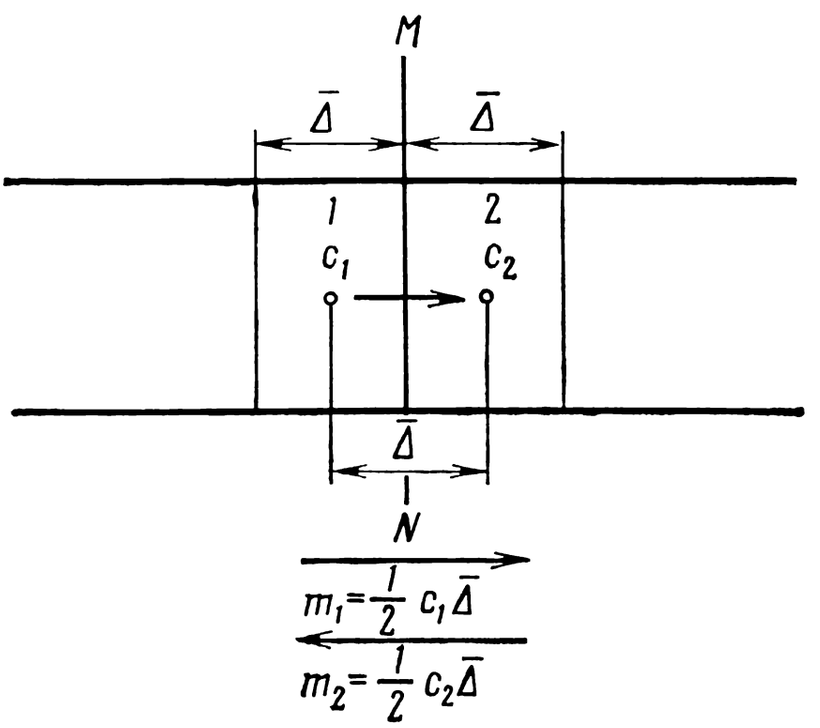

Fig. 3.4. Diagram explaining the relation $\bar{\Delta} = f(D)$

If there is a relation between Brownian motion and diffusion, there should also be a relationship between the root-mean-square value of the projection of displacement of a particle $\bar{\Delta}$ and the diffusion coefficient D. This relationship was established independently by Einstein (1905) and Smoluchowski (1906).

To establish the relationship $\bar{\Delta} = f(D)$, let us simplify Einstein's reasoning given in one of his works. As was the case with the derivation of Einstein's equation, let us suppose that a tube (see Fig. 3.4) has a cross-section of s cm^2 and is filled with a colloidal solution whose concentration uniformly diminishes from left to right. Of course, this is also the direction in which colloidal particles will diffuse. Let us imagine now that there are two solution layers *1* and *2* in this tube which have average concentrations of the solute c_1 and c_2 that correspond to the concentrations of the substance in the centres of the layers *1* and *2*. Let $\bar{\Delta}$ be the root-mean-square value of the projection of displacement of a particle on the axis parallel to the direction of diffusion in time τ.

Owing to chaotic Brownian motion, the transfer of any particle of a solute is probably equal to the right and to the left. The mass of a substance transferred in time τ across the imaginary plane MN to the right will be $m_1 = c_1\bar{\Delta}s/2$, and to the left, $m_2 = c_2\bar{\Delta}s/2$. Apparently, as a result of both of these processes, the quantity of a substance which has diffused through the plane MN from left to right will be expressed by the equation

$$m = m_1 - m_2 = \frac{c_1\bar{\Delta}s}{2} - \frac{c_2\bar{\Delta}s}{2} = \frac{\bar{\Delta}(c_1 - c_2)s}{2} \tag{3.16}$$

But it follows from Fig. 3.4 that

$$\frac{c_1 - c_2}{\bar{\Delta}} = -\frac{dc}{dx} \tag{3.17}$$

or

$$c_1 - c_2 = -\bar{\Delta}\frac{dc}{dx} \tag{3.18}$$

Substituting Eq. (3.18) in Eq. (3.16), we obtain

$$m = -\frac{1}{2}\bar{\Delta}^2\frac{dc}{dx}s \tag{3.19}$$

Combining Eq. (3.19) and Fick's equation ($m = -Ds\tau\, dc/dx$), we have

$$D = \bar{\Delta}^2/(2\tau) \tag{3.20}$$

or

$$\bar{\Delta} = \sqrt{2D\tau} \tag{3.21}$$

Hence the conclusion that the quantity $\bar{\Delta}$ and, consequently, displacement itself are proportional not to τ but to $\sqrt{\tau}$.

Inserting the value of D from Einstein's equation (3.13) in Eq. (3.21) we obtain

$$\bar{\Delta} = \sqrt{\frac{RT2\tau}{N_A 6\pi\eta r}} = \sqrt{\frac{kT\tau}{3\pi\eta r}} \tag{3.22}$$

This equation is known as the Einstein-Smoluchowski equation.

Svedberg checked the Einstein-Smoluchowski equation, examining gold sols under the ultramicroscope. He determined the values of $\bar{\Delta}$ at different time intervals and calculated the theoretical values of $\bar{\Delta}$ by the formula $\bar{\Delta} = \sqrt{k_1\tau}$, where $k_1 = kT/(3\pi\eta r)$. The results which he obtained for a gold sol with particles having a diameter of 0.044 μm are given below:

Observation time, sec	1	2	3	4
Value of $\bar{\Delta}$, μm				
experimental	4.3	5.8	6.6	8.3
estimated	4.1	5.8	7.6	8.2

The results coincided quite satisfactorily. Similar results were obtained by Svedberg with other objects, and also by other scientists.

Moreover, in order to check the Einstein-Smoluchowski equation, Svedberg determined the dependence of $\bar{\Delta}$ on the viscosity of the dispersion medium of a colloidal system. In this case, he used the formula $\bar{\Delta} = \sqrt{k_2/\eta}$, where $k_2 = kT\tau/(3\pi r)$, to calculate the theoretical value of $\bar{\Delta}$.

Seddig checked the Einstein-Smoluchowski equation by determining the dependence of $\bar{\Delta}$ on temperature. He calculated the theoretical values of $\bar{\Delta}$ by the equation $\bar{\Delta} = \sqrt{k_3 T/\eta}$, where $k_3 = k\tau/(3\pi r)$. The right-hand member of this equality has the quantity η because the viscosity of the dispersion medium changes with temperature. Experiment has supported the theory in this case as well.

The Avogadro number may be calculated by using the Einstein-Smoluchowski equation and knowing the value of $\bar{\Delta}$ and all the other quantities. This was done by Perrin who carried out experiments with the gamboge suspension. The Avogadro number which he calculated was equal to 6.8×10^{23} which is close to the values of N_A determined by other methods (6.02×10^{23}).

Perrin found the value of the Avogadro number by observing not only the translatory, but also rotary, motion of visible microscopic particles. A particle rotates under the action of impacts which the molecules of a medium communicate to it. As Einstein has shown, this rotary motion obeys the equation

$$\theta = \sqrt{\frac{RT}{N_A} \cdot \frac{\tau}{4\pi\eta r^3}} \qquad (3.23)$$

where θ is the root-mean-square of the angular displacement of a particle in time τ.

Perrin obtained the value of 6.5×10^{23} for the Avogadro number by examining the rotation of relatively large particles of the mastic suspension under the microscope and using Eq. (3.23).

The investigation of Brownian motion and diffusion in colloidal systems was not only an important factor in understanding the nature of disperse systems and establishing the community of molecular-kinetic properties of such systems and of molecularly dispersed ones, but was also proof of the molecular-kinetic theory as a whole. The theory of Brownian motion, worked out by Einstein and Smoluchowski, confirmed the existence of molecules exactly when a heated discussion was being held on this question. W. Ostwald and other representatives of the energy school argued that the use of the concepts of the atom and the molecule should be avoided; they thought that objective reality was not to be found behind these words.

Hence, the importance of the theory of Brownian motion is not

confined to colloid chemistry where it was, incidentally, the first quantitative theory. The theory of Brownian motion, according to which the motion of colloidal particles is the direct result of the thermal motion of molecules, has become very important in physical chemistry, physics, and even philosophy, being conclusive evidence that the materialistic view of the world is correct. The investigation of Brownian motion has led to the creation of the fluctuation theory and promoted the development of statistical physics.

Fluctuations are spontaneous deviations of a parameter from the mean equilibrium value in sufficiently small volumes of a system. Fluctuations are undergone by physical quantities (e.g., density, concentration), biological quantities (growth, lifetime), socio-economic quantities (population density in a given place, the price of merchandise), and so forth. The fundamentals of the general fluctuation theory were elaborated by the American scientist Gibbs (1902).

The simplest way of observing fluctuations in a colloidal system is by determining the number of particles in a microscopically small volume at equal lengths of time. For example, Svedberg calculated the number of particles in 1000 μm^3 of a gold sol in this way, and obtained the following series of values: 1, 2, 0, 0, 2, 0, 0, 1, 3, etc. He made 518 observations in all. The number of particles in the isolated volume averaged 1.545, but at separate moments it dropped to zero or rose to seven.

The inconformity of the number found to the average value may be explained only by the fact that the chaotic motion of particles causes sometimes a large and sometimes a small number of particles to get randomly into the microvolume. Of course, if a sufficiently large volume containing an enormous number of particles were taken instead of the microvolume, the average numerical concentration in such a macrovolume would turn out to be constant as a result of compensation of the excess of particles in some of its regions by the insufficiency of particles in others.

It follows that fluctuation is a phenomenon which is, as it were, the opposite of the diffusion although both of them are caused by thermal motion. In diffusion, concentrations are equalized in macrovolumes, whereas fluctuations are a spontaneous deviation of concentration from its average value in microvolumes.

We will not consider the fluctuation theory in this textbook. It should only be noted that in respect to colloidal systems, the theory makes it possible to estimate the probability of different numerical concentrations in microvolumes, and also to find the length of time at which a given concentration will be repeated again in the isolated volume. This length of time usually grows sharply as the deviation of concentration from the average value increases. For example, estimates show that, in 1 ml of gas under standard conditions, the numerical concentration will deviate by

1 per cent in 10^{180} years, i.e., this deviation is virtually impossible. However, such an occurrence is not absolutely impossible, as is characteristic of the second principle of thermodynamics which is of a statistical nature.

3. OSMOTIC PRESSURE

Osmotic pressure π of sufficiently diluted colloidal solutions may be found by the equation

$$\pi = \frac{m_{tot}/m}{VN_A} RT = \nu \frac{RT}{N_A} = \nu kT \tag{3.24}$$

where m_{tot} = mass of the solute;
m = mass of the particle;
V = volume of the system;
N_A = Avogadro number;
T = absolute temperature;
ν = numerical concentration.

This equation is similar to the well-known van't Hoff equation for the osmotic pressure of true solutions

$$\pi = \frac{m_{tot}/M}{V} RT = \frac{c}{M} RT \tag{3.25}$$

where M = mass of one mole of the solute;
c = weight concentration.

Molecular-kinetic equations which are suitable for true solutions can be applied also to colloidal solutions, the only difference being that the mass of a mole of a substance is replaced by the mass of particles in them.

Osmotic pressure of lyosols is distinguished from that of true solutions by its small value and inconstancy. It becomes clear why lyosols have low osmotic pressure from the explanation presented below.

For two systems having osmotic pressures π_1 and π_2 and the same temperature, we may write

$$\pi_1 = \nu_1 (RT/N_A) \tag{3.26}$$

$$\pi_2 = \nu_2 (RT/N_A) \tag{3.27}$$

Dividing Eq. (3.26) by Eq. (3.27), we obtain

$$\pi_1/\pi_2 = \nu_1/\nu_2 \tag{3.28}$$

It follows from this equation that the osmotic pressure of a disperse system is determined only by the numerical concentration and does not depend on the nature and dimensions of particles. This equation also explains the low osmotic pressure of any colloidal system

since, owing to the large mass of colloidal particles of the same gravimetric concentration, the numerical concentration of a colloidal system is always far less than that of a true solution. Very low osmotic pressure of lyosols was the cause of the error made by T. Graham who did not have sensitive osmometers and who believed that osmotic pressure was absent altogether from colloidal solutions.

The second feature of osmotic pressure of lyosols, i.e., its inconstancy, is due to the phenomenon of aggregation which is characteristic of colloidal systems. For two colloidal systems which have a dispersed phase of the same nature and the same gravimetric concentration c, but which differ from one another by the particle dimensions, we may write

$$\frac{\pi_1}{\pi_2} = \frac{\nu_1}{\nu_2} = \frac{c/(4/3\pi r_1^3\rho)}{c/(4/3\pi r_2^3\rho)} = \frac{r_2^3}{r_1^3} \tag{3.29}$$

where r_1 and r_2 = radii of particles of the first and second systems;
ρ = density of the dispersed phase.

According to this equation, the ratio between osmotic pressures of two such systems is inversely proportional to the ratio between the cubed radii of their particles. It follows that even a small change in the particle radius causes a great change in osmotic pressure. Obviously, osmotic pressure must sharply drop with an increase in the average radius of the particles as a result of their agglomeration and the formation of aggregates. Conversely, osmotic pressure must greatly increase as aggregates disintegrate to primary particles. Since aggregation and disaggregation in colloidal systems readily occur under the action of sometimes even very weak external effects, it is clear why osmotic pressure of lyosols is inconstant and why it depends on the prehistory of a solution.

Owing to the low value and inconstancy of osmotic pressure of lyosols, such methods as osmometry, ebullioscopy, and cryoscopy are not used for determining the numerical concentration or dimensions of colloidal particles. These methods cannot be used for determining the dimensions of colloidal particles also owing to the presence of electrolytes in lyosols. In purifying lyosols, say by dialysis, a stabilizing electrolyte may be removed together with extraneous electrolytes; this upsets the aggregate stability of a system, enlarges particles, and consequently leads to incorrect values of osmotic pressure. In addition, the "membrane equilibrium", or the Donnan equilibrium, strongly affects the results of osmometric determinations. This equilibrium is established upon a complicated distribution of ions between a colloidal solution in the osmotic cell and an extraneous solution; this will be considered in detail in Chap. 14.

However, osmometry is quite applicable for determining the molecular weight of high molecular weight substances which form

true solutions and do not require the presence of electrolytes in solutions for their stabilization. This determination may be made because solutions of high molecular weight substances may be obtained at a sufficiently high concentration; they are, as a rule, quite stable aggregatively and withstand purification operations well.

4. SEDIMENTATION STABILITY

In considering diffusion, we do not take account of the effect of the gravitational field (the earth's attraction) on a system. However, this is necessary for particles of a rather large mass because they will settle, or *sediment*, under the action of the gravitational field. As a result, definite equilibrium distribution of particles along the height is established in a system, or particles precipitate if they are heavy enough.

The ability of a disperse system to maintain uniform distribution of particles throughout the volume is known as the *sedimentation* or *kinetic stability* of a system. Apparently, it would be expedient to deal with sedimentation stability or instability only when considering freely dispersed systems where every particle is free and is in thermal motion.

Coarsely dispersed systems (e.g., dust or the suspension of sand in water) have low kinetic stability and sediment because their particles are heavy and can hardly effect thermal (Brownian) motion. Conversely, highly dispersed systems (gases, true solutions) possess high kinetic stability because they are characterized by thermal motion and diffusibility. Colloidal systems (aerosols, lyosols) hold an intermediate place by their stability.

The distribution of particles, which have the same dimensions and are visible under the microscope or the ultramicroscope, along the height can be studied by two methods. In the first case, the microscope is set horizontally and is moved along the height when a system is being studied. Then, one immediately sees that the number of particles decreases with the height. According to the second, more widely used, method, the microscope is set vertically in an examination so that only the particles in the layer on which the microscope is focussed are seen. The thickness of this layer in experiments carried out by Perrin who worked with monodispersed gamboge sols was ca. 1 μm. By raising or lowering the drawtube, the microscope could be focussed on layers which were above or below the initial layer. In a series of his experiments, particles totalled 13,000 and their diameter was 0.212 μm; then the ratio between the number of particles in layers that were away from the cuvette bottom by 5, 35, 65 and 95 μm constituted 100 : 47 : 22.6 : 12. As we see, the number of particles in the field of vision of the microscope

halved after every 30 μm. In other words, as the height increased arithmetically the number of particles decreased geometrically. Consequently, as Perrin assumed, particles suspended in a liquid are distributed along the height in the gravitational field according to the same barometric formula as that for gas molecules. Perrin was awarded the Nobel Prize in 1926 for these experiments which were crowned with the complete victory of atomism and were characterized by exceptional precision, elegance and simplicity.

A comparison of the diffusion flow with the sedimentation flow directed against it is a convenient method for studying how diffusion or sedimentation affects the kinetic stability of a disperse system.

As we have seen, density of diffusion flow i_d is expressed by Eq. (3.3)

$$i_d = -D\, dc/dx$$

Density of sedimentation flow i_s, taking into account that the friction force Bu is equal to the motive force (gravity) mg for a particle that settles at a constant rate, may be represented by the equation

$$i_s = uc = (mg/B)\, c \tag{3.30}$$

where u = sedimentation rate;
c = concentration;
m = effective mass of a particle;
g = acceleration of gravity;
B = coefficient of friction between a colloidal particle and the dispersion medium.

Dividing Eq. (3.30) by Eq. (3.3) and using Eq. (3.12), we obtain

$$\frac{i_s}{i_d} = -\frac{mg}{kT} \cdot \frac{c}{dc/dx} = -\frac{v(\rho - \rho_0)\, g}{kT} \cdot \frac{c}{dc/dx} \tag{3.31}$$

where v = particle volume;
ρ and ρ_0 = density of the dispersed phase and the dispersion medium.

When $i_s/i_d \gg 1$, account may be taken of only sedimentation; when $i_s/i_d \ll 1$, only diffusion, and when $i_s/i_d \approx 1$, i.e., $i_s \approx i_d$, both processes are important. In the last case, a definite distribution of the dispersed phase along the height is established in a system.

It also follows from Eq. (3.31) that if we consider the stability of a system in which the dispersed phase is uniformly distributed throughout the volume (for example, after preliminary stirring), sedimentation always prevails at first when $dc/dx = 0$. However, the uniform distribution of a substance in a system is upset in the course of time and the derivative dc/dx increases. Mass transfer will continue until flow i_d becomes equal to i_s, i.e., until the condition $i_s/i_d = 1$ is met and equilibrium is established in a system. Taking into account that the concentration gradient changes with height

and substituting h for x, Eq. (3.31) may be written as

$$-\frac{mg}{kT}\cdot\frac{c}{dc/dh}=1$$

This equation may be written as

$$-\frac{dc}{c}=\frac{mg}{kT}\,dh \tag{3.32}$$

Integrating from c_0 to c_h and, accordingly, from 0 to h, we obtain

$$\ln\,(c_0/c_h)=mgh/kT=mN_Agh/RT \tag{3.33}$$

or

$$c_0/c_h=\exp\left(\frac{mgh}{kT}\right) \tag{3.34}$$

If the quantity c in Eq. (3.33) is replaced by its proportional quantity of pressure p, we will obtain the well-known barometric formula

$$\ln\,(p_0/p_h)=mgh/kT \tag{3.35}$$

This is the *hypsometric law*, obeyed by the distribution of gas molecules along the height.

Since the concentration of the dispersed phase c is proportional to the numerical concentration ν, Eq. (3.33) may be represented as

$$\ln\,(\nu_0/\nu_h)=mgh/kT \tag{3.36}$$

This equation may be rewritten as follows:

$$h=\frac{kT\ln\,(\nu_0/\nu_h)}{mg} \tag{3.37}$$

It is convenient to use this formula to calculate the quantity h for any freely dispersed system; this quantity represents the height which must be attained for the numerical (or, accordingly, gravimetric) concentration to decrease from ν_0 to ν_h or by ν_0/ν_h times.

Table 3.2. **Diminution in the Concentration of a Substance with Height in Various Disperse Systems**

System	Particle diameter, nm	Height h (in cm) at which concentration diminishes	
		twice	10^6 times
Oxygen	0.27	500,000 (5 km)	10,000,000 (100 km)
Gold sol	1.86	215	4300
Ditto	8.35	2.5	50
Ditto	186	2×10^{-5} (0.2 μm)	4×10^{-4} (4 μm)
Gamboge suspension	230	3×10^{-3} (30 μm)	6×10^{-2} (600 μm)

Table 3.2 gives the quantities of h calculated by Eq. (3.37) at $(\nu_0/\nu_h) = 2$ and $(\nu_0/\nu_h) = 10^6$.

Table 3.2 shows that the value of h sharply drops as the mass (diameter) of particles increases. The value of h is higher for the gamboge suspension with particles whose diameter is 230 nm than for the gold sol with particles whose diameter is 186 nm because the density of gold is many times greater than that of gamboge.

Of course, the distribution of particles along the height which obeys the hypsometric law is realized only in monodisperse systems. In polydisperse systems, distribution is far more complicated. Data concerning the effect of Brownian motion and sedimentation on the rate of movement of particles in a polydispersed silver hydrosol are given below

Particle diameter, μm	0.1	1	10
Distance passed by a particle in 1 sec, μm			
as a result of Brownian motion	10.0	3.1	1.0
as a result of sedimentation	0.0676	6.75	676.0

By comparing the rates of Brownian motion and sedimentation, we can see that silver particles whose diameter is smaller than 0.1 μm are more or less uniformly distributed throughout the volume of a system, silver particles whose diameter is greater than 10 μm are found mainly in the precipitate, and particles of intermediate dimensions are distributed along the height according to the hypsometric law, and every fraction has its own equilibrium.

Although, according to the hypsometric law, sol concentration should decrease very rapidly with the height, disperse systems often reveal almost the same concentration along the height of a column. This is especially characteristic of highly dispersed sols. Such a phenomenon is explained by the fact that, as the particle dimensions diminish, gravity causing sedimentation decreases far more rapidly than friction because gravity for spherical particles is proportional to the third power of the particle radius whereas friction is proportional to the first power of the radius. As a result, equilibrium at which the hypsometric law may be applied establishes very slowly for highly dispersed sols; we deal mainly with systems where the distribution of particles along the height greatly differs from theoretical distribution.

To illustrate the effect of the particle dimensions on the sedimentation rate, we give on p. 80 the rates of sedimentation of spherical quartz particles in water as a function of their radius (for SiO_2, $\rho = 2.7$ g/cc, for H_2O, $\eta = 0.015$ P).

The equilibrium distribution of particles in a system is affected by the slightest jolt and shock and by different temperatures in various regions of a sol, because it provokes convection flows in the system. It is

enough, for example, for temperature to fluctuate by 0.001 °C per hour to completely exclude sedimentation in the highly dispersed gold sol.

Particle radius, cm	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}
Sedimentation rate, cm/sec	3.2×10^{-2}	3.2×10^{-4}	3.2×10^{-6}	3.2×10^{-8}	3.2×10^{-10}
Time required for the sedimentation of a particle by a distance of 1 cm	31 sec	51.7 min	86.2 hrs	359 days	100 years

Nevertheless, the hypsometric law for lyosols is obeyed quite precisely under the conditions of equilibrium distribution of particles in a system. Evidence of this is the fact that Perrin was able to calculate the Avogadro number from the equilibrium distribution of relatively large particles of the monodispersed gamboge suspension along the height which he established by means of a microscope. The value of N_A thus found was equal to 6.82×10^{23}, rather close to the value found by other methods. Westgren worked with gold sols and obtained an even more precise value of the Avogadro number: 6.05×10^{23}. Westgren obtained equilibrium during both the sedimentation of a substance and its diffusion from the bottom of a vessel.

5. SEDIMENTATION AND METHODS OF SEDIMENTATION ANALYSIS

It is comparatively easy and convenient to determine the particle dimensions by observing the sedimentation rate in suspensions, i.e., in disperse systems having sufficiently large particles which possess almost complete kinetic instability. This is done by the methods of *sedimentation analysis.*

Let us see how a particle of such a suspension sediments in a liquid.

A particle sediments apparently under the action of gravity f which, with regard to the loss in weight according to Archimedes' law, constitutes

$$f = v(\rho - \rho_0)\, g$$

where v = particle volume;
ρ = density of the particle substance;
ρ_0 = density of the medium;
g = acceleration of gravity.

Sedimentation is counteracted by the friction force $f' = Bu$, where B is the coefficient of friction between a particle and the medium, and u is the rate of sedimentation of a particle.

At first, a particle moves rapidly because gravity is greater than the friction force at low rates. As the rate of motion increases, the friction force grows and at a certain moment counterbalances gravity, owing to which the particle begins to move at a constant rate. Under steady-state conditions of sedimentation, the following equality should be observed:

$$v(\rho - \rho_0) g = Bu \tag{3.38}$$

When this equation is applied to spherical particles, it assumes the form

$$^4/_3\pi r^3 (\rho - \rho_0) g = 6\pi\eta r u \tag{3.39}$$

From Eq. (3.39), it is easy to find the rate of sedimentation of a particle:

$$u = \frac{2r^2}{9\eta} (\rho - \rho_0) g \tag{3.40}$$

According to Eq. (3.40), the rate of sedimentation of a particle is directly proportional to the square of the radius (or diameter) of a particle and inversely proportional to the viscosity of a medium, and depends on the difference of $\rho - \rho_0$: at $\rho > \rho_0$, sedimentation occurs; at $\rho < \rho_0$ (e.g., a suspension of paraffin in water), particles rise to the surface, i.e., a phenomenon opposite to sedimentation is observed.

It is easy also to find the radius of a particle from Eq. (3.39), when the rate of its sedimentation and the values of the quantities η, ρ and ρ_0 are known:

$$r = \sqrt{\frac{9\eta u}{2(\rho - \rho_0) g}} \tag{3.41}$$

Equation (3.39) is valid for aqueous suspensions having particles whose size is 0.1-100 μm because, for these particles, the time during which the sedimentation rate grows to a constant value is so small that it does not affect the results of sedimentation analysis. For example, the time during which quartz particles having a radius of 50 μm attain a constant sedimentation rate in water is 3.4×10^{-3} sec, and for particles having a radius of 1 μm, it is only 1.7×10^{-6} sec.

Eq. (3.39) is inapplicable to particles whose radius is larger than 100 μm and which sediment rapidly under standard conditions, and to particles whose radius is less than 0.1 μm and which are found in kinetically stable systems. In these cases ordinary sedimentation analysis is useless.

Let us now consider the sedimentation of disperse systems which consist of many particles. Let us assume that these particles sediment independently of one another.

In a monodisperse system, sedimentation is uniform (the height of the layer of clarified liquid is proportional to sedimentation time τ)

because the sedimentation rates of particles equal in dimensions are the same. Here, the interface between the concentrated suspension that has settled and the clear medium shifts by a certain distance. The sedimentation rate is expressed by the equation

$$u = H/\tau \tag{3.42}$$

and the particle radius is expressed by the equation

$$r = k\sqrt{H/\tau} \tag{3.43}$$

where

$$k = \sqrt{\frac{9\eta}{2(\rho - \rho_0)g}}$$

The radius of particles of a suspension may be easily calculated from the results of the visual observation of its sedimentation by Eq. (3.43). The sedimentation rate of a monodispersed suspension may be determined by observing the sedimentation of one of its particles under the microscope.

During sedimentation of a polydispersed suspension, unlike a monodispersed one, the boundary of the sedimenting layer is diffused because particles having various radii pass different distances in the same length of time. Therefore, the sedimentation analysis of a polydisperse system consists in the determination of the rate of accumulation of a precipitate.

The techniques of establishing the relationship between the mass of a precipitate m and the sedimentation time τ, graphically represented by the *sedimentation curve* which gives the data for characterizing the polydispersion of a test system, are considered at length in courses in practical colloid chemistry. In calculating the particle dimensions from the sedimentation curve that characterizes the content of particles of different dimensions in polydisperse systems, the analytical methods of plotting sedimentation curves, elaborated by N. Avdeyev and N. Tsyurupa, are used along with the classical graphic method of calculation proposed by S. Oden.

A distribution curve which shows the weight content Q of various fractions in a suspension is usually plotted according to the results obtained when the sedimentation curve is being interpreted. To this end, a diagram is drawn, and the values of particle radii r are plotted on the abscissa, whereas those of $Q/\Delta r$ for each fraction, on the ordinate. An example of such a diagram is given in Fig. 3.5. Then, $Q\Delta r/\Delta r = Q$, and the weight content of each fraction will be expressed by the area of the corresponding rectangle. The distribution curve is obtained by constructing such rectangles for all fractions and uniting the central points of their upper sides with a smooth line. The fraction that corresponds to the maximum of the distribution curve is known as the main fraction of a polydispersed suspension because it is evident that particles constituting this fraction are

the most in the system (in Fig. 3.5, this fraction is IV with particles whose radius is in the r_4-r_5 range).

Distribution curves are an important characteristic of dispersed systems. The narrower the interval of the radii of the distribution

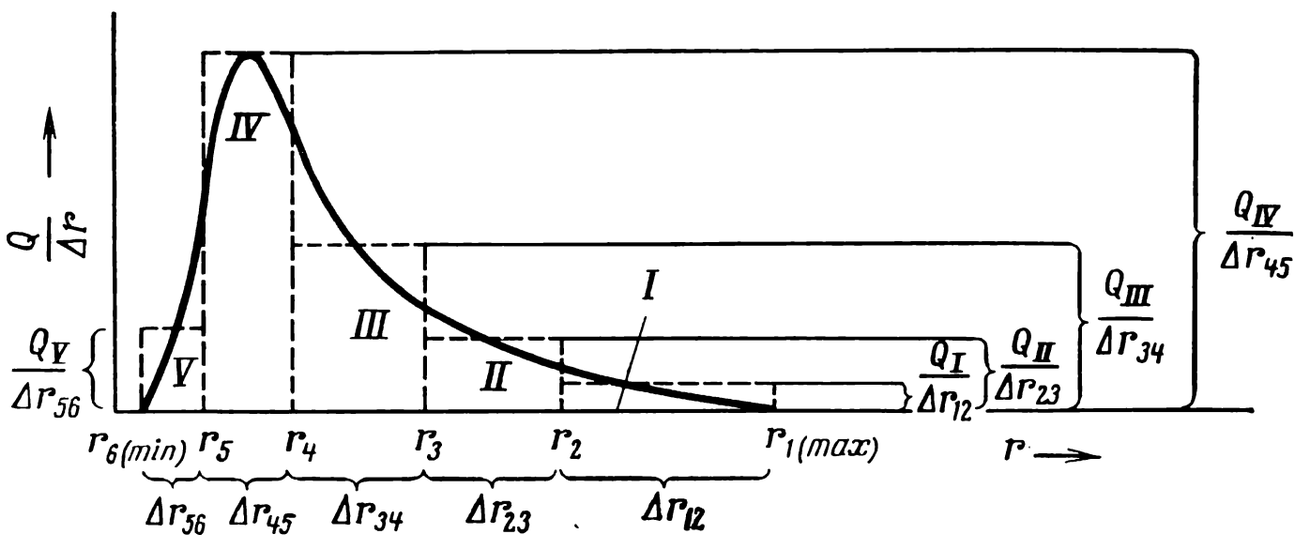

Fig. 3.5. Plotting the distribution curve

curve and the higher its maximum, the closer is a suspension to a monodispersed one. Conversely, the broader the curve and the lower the maximum, the more polydispersed is the suspension. Fig. 3.6 gives four different types of distribution curves.

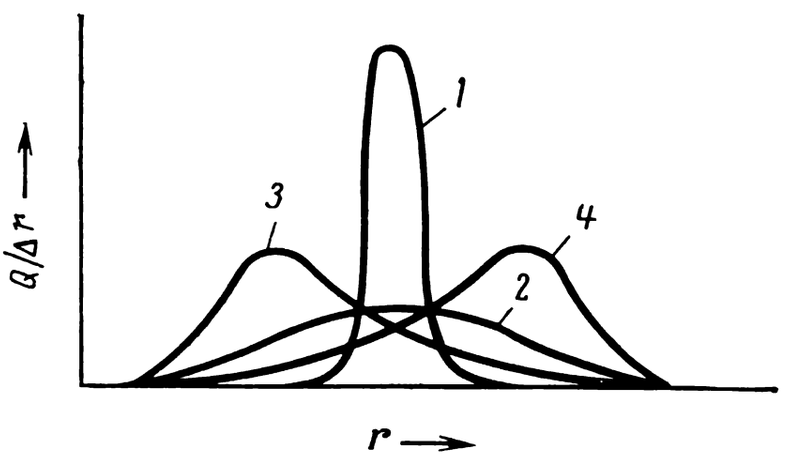

Fig. 3.6. Typical distribution curves:
1—system which most approximates a monodispersed one; *2*—system which most approximates a polydispersed one; *3*—system containing mainly fine particles; *4*—system containing mainly coarse particles

Let us now briefly treat experimental techniques used in the sedimentation analysis of polydispersed systems.

The gravimetric modification of sedimentation analysis consists in the determination of the rate of accumulation of a precipitate on the balance pan. For this purpose, sedimentation balances of diverse designs were proposed. One of widely used sedimentation balances is the device which N. Figurovsky proposed in 1936. This device

(Fig. 3.7) consists of a flexible glass or quartz spike *2* which is fixed horizontally in the holder of stand *1* and on whose end a thin-walled glass cup *3* is suspended with a glass thread. The distance between the liquid surface and the suspended cup is denoted by *H*. When the cup is in the cylinder with the test suspension, a precipitate gradually accumulates on the cup and the spike sags. This sagging is observed by means of the measuring microscope. The graph of

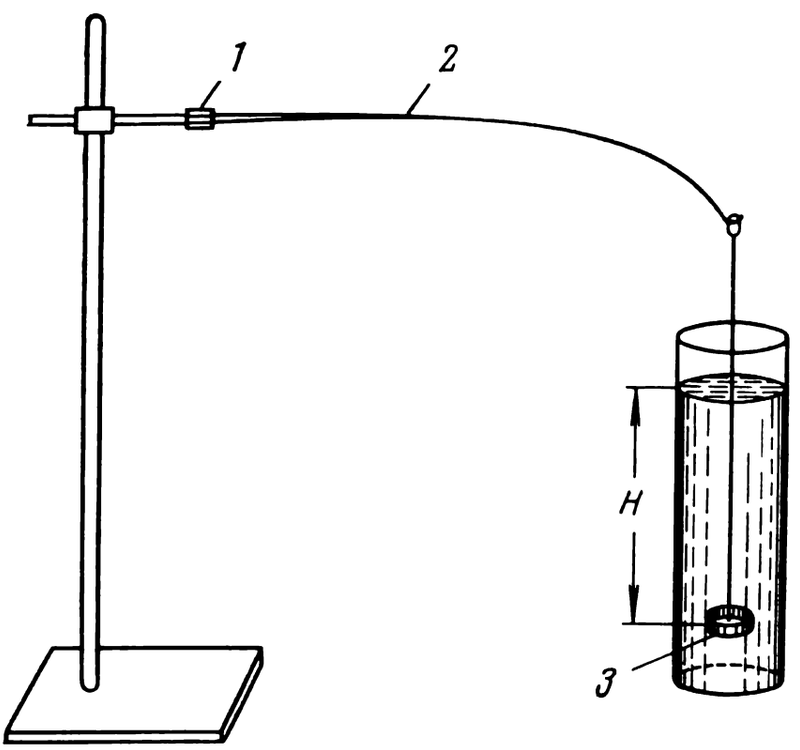

Fig. 3.7. Figurovsky's sedimentometer:
1—stand holder; *2*—spike; *3*—cup

a change in the extent of spike sagging over time is plotted by recording the movement of the spike end along the microscale. Since spike sagging obeys Hooke's law, the graph expresses the dependence of the precipitate mass m on time τ, i.e., $m = f(\tau)$. The cup may be fixed to the beam of the torsion balance instead of being suspended on the end of the flexible spike, and the accumulation of the precipitate is determined by the movement of the pointer on the balance dial.

Another method of observing the course of sedimentation of polydispersed systems was proposed by Wigner in 1918. This method is based on the measurement of the hydrostatic pressure of the suspension column when the dispersed phase has separated from the suspension as a result of sedimentation. Measurements by this method are made in a special device, known as Wigner's sedimentometer (Fig. 3.8). When the stopcock which connects both elbows of the device is closed, the suspension is poured into the wide tube *1* and the dispersion medium is introduced into the narrow tube *2*; then the stopcock is opened. At first, the liquid level in tube *2* is higher than that in tube *1* because the average density of a suspension is

usually greater than the density of a medium. However, as the dispersed phase of the suspension settles and the sediment accumulates on the bottom of tube *1*, the density of the suspension will gradually approximate that of the medium, and h, the difference in liquid levels in the two elbows, will decrease. The dependence of h on sedimentation time may be used to plot the sedimentation curve.

Another method of sedimentation analysis was worked out by N. Figurovsky and T. Gavrilova, but it requires rather intricate equipment. For sedimenting the dispersed phase, these authors have designed automatic centrifugal devices which make it possible to determine the dimensions of particles of highly dispersed systems (to 0.05 μm when the density of the dispersed phase is 2-4 g/cc), to study the kinetics of sedimentation of particles, and to obtain then the curve of distribution of particles according to their dimensions.

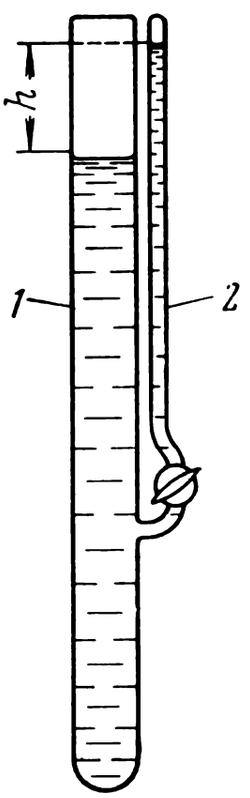

Fig. 3.8. Wigner's sedimentometer: *1*—tube with the suspension; *2*—tube with the dispersion medium

Several conditions which restrict the applicability of sedimentation analysis should be noted. First of all, the main equation of this analysis (3.39) may be used only for calculating the dimensions of spherical particles. For particles which are not spherical, Eq. (3.39) makes it possible to determine only the *effective* or *equivalent radius*, i.e., the radius of imaginary spherical particles which possess the same density and sediment at the same rate as the suspension particles. Second, in sedimentation analysis, correct results may be obtained with the aid of Eq. (3.39) only when particles are not solvated. Of course, the effect of solvation will be the greater, the smaller is the particle size. Third, sedimentation analysis may be used only when particles settle separately from one another (when the concentration of a system is not too high) and when they do not form aggregates.

Ultracentrifuge and its application in dispersion analysis. Only sufficiently coarse particles sediment under the action of the gravitational field. Colloidal particles either do not sediment at all or settle very slowly under the action of gravity. For example, quartz particles having a radius of 0.1 μm pass 1 cm in 86.2 hours in sedimentation.

However, colloidal particles may also be made to sediment rapidly if the gravitational field is replaced by the action of a centrifuge whose acceleration is hundreds of thousands of times greater than the acceleration of gravity. For example, in a centrifugal field having an acceleration of 10^5 *g*, the same quartz suspension sediments by 1 cm in only three seconds.

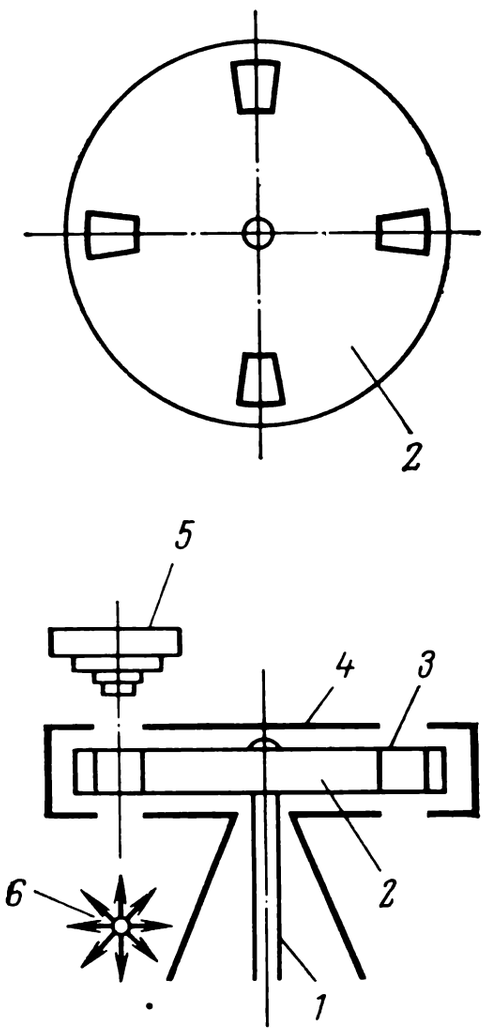

Fig. 3.9. Schematic diagram of the ultracentrifuge:
1—axis; *2*—rotor; *3*—quartz cuvettes; *4*—casing; *5*—camera; *6*—light source

In 1910 the Russian scientist A. Dumansky proposed to use, for the first time, the ultracentrifuge for determining the dimensions of colloidal particles. The Swedish scientist T. Svedberg worked out several designs of the ultracentrifuge for determining the dimensions of colloidal particles and molecules of high molecular weight substances, such as proteins.

A schematic diagram of the ultracentrifuge is given in Fig. 3.9. The centrifuge axis *1* to be set in motion has rotor *2* which is a bulky disc with radial grooves. Strong quartz cuvettes *3* are placed into the grooves, and the test colloidal system is poured into the cuvettes. The rotor of the ultracentrifuge which rotates at a very high speed (tens of thousands of revolutions per minute) is surrounded by casing *4*. The casing has openings which correspond to the rotor grooves. Light source *6* is fixed under the lower opening of the casing, and camera *5*, above the upper opening. After rotation for a long time, colloidal particles are thrown to the periphery by the centrifugal force if their density is greater than that of the medium. As a result, a concentrated sol layer appears closer to the periphery of the cuvette, and a clarified liquid layer, closer to the rotation axis. In the course of centrifugation, the first layer decreases and the second one increases until sedimentation equilibrium is established or until all the particles sediment to the bottom. The movement of the interface of the two layers may be traced by photographing it at definite time intervals. These photographs are schematically shown in Fig. 3.10.

In the centrifugation of a polydispersed system, a distinct boundary is not formed. However, photographs make it possible to establish the distribution of concentrations of the dispersed phase in the cuvette.

In investigating colourless and transparent sols, the shift of the interface or the distribution of concentrations in a cuvette is determined not by photography, but by measuring the refraction index of a sol in various regions of the cuvette.

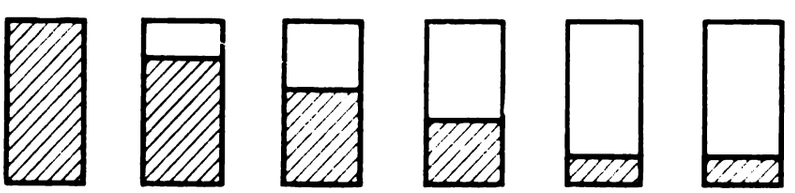

Fig. 3.10. Displacement of the interface between the sol and the dispersion medium in the ultracentrifuge cuvettes during centrifugation

The data obtained may be used to calculate the sedimentation rate or to find sedimentation equilibrium. Proceeding from this, it is possible to calculate the molecular weight or the dimensions of sedimenting particles.

Let us consider in greater detail the determination of the dimensions of particles according to the rate of their sedimentation in the ultracentrifuge. For calculations, we may use the equation which is similar to the ordinary sedimentation equation (3.38). However, since the particles in centrifugation move away from the rotation axis at an ever growing rate, the quantity u in the equation should be replaced by $dx/d\tau$, where x is the distance of a particle from the rotation axis. We know from mechanics that acceleration in the centrifugal field is $\omega^2 x$, where ω is the angular velocity. Then, Eq. (3.38) as applied to ultracentrifuging may be written as

$$B\,dx/d\tau = v\,(\rho - \rho_0)\,\omega^2 x \tag{3.44}$$

Dividing the variables and integrating from x_1 to x_2 and, accordingly, from 0 to τ, we obtain

$$\int_{x_1}^{x_2} dx/x = \frac{v\,(\rho - \rho_0)\,\omega^2}{B} \int_0^{\tau} d\tau$$

$$\ln\,(x_2/x_1) = v\,(\rho - \rho_0)\,\omega^2\tau/B \tag{3.45}$$

Assuming that the particles are spherical and substituting the respective values for B, we obtain

$$\ln\,(x_2/x_1) = 2r^2\,(\rho - \rho_0)\,\omega^2\tau/(9\eta) \tag{3.46}$$

In solving this equation with respect to r, we may write

$$r = \sqrt{\frac{9\eta \ln (x_2/x_1)}{2(\rho - \rho_0)\omega^2 \tau}} \tag{3.47}$$

Using Eq. (3.47), the numerical or molecular weight may be calculated from the movement of spherical particles in the ultracentrifugal field by a distance of $(x_2 - x_1)$ in time τ. Of course, for this purpose, it is necessary to know also the quantities η, ρ, ρ_0, and ω.

Eq. (3.45) may be represented such that its right-hand member has all the constants which characterize the system under consideration:

$$\frac{\ln (x_2/x_1)}{\tau\omega^2} = \frac{v(\rho - \rho_0)}{B} = \frac{m}{B} = \text{const} \tag{3.48}$$

The expression $\ln (x_2/x_1)/(\tau\omega^2)$ is known as the *sedimentation constant* and is denoted by S. This constant may serve as a measure of the "sedimentation ability" of a given system.

If the diffusion coefficient is known, we can eliminate B from the relation $D = kT/B$ for diffusion and from equation $S = m/B$, and then find the mass m and, consequently, the numerical or molecular weight. Such a technique of determining the numerical or molecular weight is especially suitable for systems containing particles, which greatly differ from spherical ones by their shape or which are strongly solvated, because the quantities S and D equally depend on the shape and the extent of solvation of particles.

The dimensions of colloidal particles may be found by determining not only the sedimentation rate in the ultracentrifuge, but also sedimentation equilibrium. In the latter case, the speed of rotation should not be too high (about 20,000 rpm); otherwise, sedimentation will prevail and equilibrium will not be established. The numerical or molecular weight that is found from sedimentation equilibrium conforms to the equilibrium distribution of particles in a system, but does not depend on how this distribution has been attained, consequently, the shape of particles and their solvation cannot affect the results of analysis.

By combining the determination of the sedimentation rate with that of sedimentation equilibrium, we may also find the particle distribution curve if a polydispersed system is subjected to centrifugation. A comparison of the results of sedimentation in the ultracentrifuge according to both methods also makes it possible to determine the shape of particles.

The modern ultracentrifuge is an intricate device whose design allows the rotor to rotate uniformly, without vibrations, and prevents the slightest temperature fluctuations in the cuvette. In the up-to-date ultracentrifuges, the rotor has a diameter of only several centimetres,

is made of chrome-nickel steel, and rotates in a flow of rarefied hydrogen. Hydrogen is characterized by high heat conduction; therefore, it ensures the rapid outlet of heat which is liberated as a result of friction and thus reduces the possibility of thermal convection in a cuvette. Such ultracentrifuges are put into rotary motion by means of oil turbines. There are also ultracentrifuges whose rotor is put into motion and kept in a suspended state by an air flow.

Ultracentrifuges are used not only for the determination of the numerical or molecular weight of dispersed systems, but also for preparative purposes, e.g., the separation of mixtures of high molecular weight compounds in solutions into fractions of different molecular dimensions.

4

SCIENCE OF ADSORPTION. ADSORPTION AT THE SOLID—GAS INTERFACE

1. CONCEPT OF ADSORPTION

Adsorption is the accumulation of a gas or a solute at the interface. The gas or the solute is known in this case as the *adsorptive** while the liquid or the solid which has adsorbed them, as the *adsorbent.*

Since adsorption is a surface phenomenon, it is, of course, very important to colloidal systems which have a large surface. The coagulation of lyosols, the peptization of colloidal precipitates, a change in the sign of the particle charge, and other similar phenomena, are connected very closely with adsorption.

Adsorption of gases by coal was observed by C. Scheele as early as the 18th century. The phenomenon of adsorption of substances from a solution was first noticed by the Russian scientist T. Lowitz in 1785. The Swiss scientist N. Saussure in 1814 found that all porous bodies, i.e., bodies having a large surface, are capable of adsorbing gases, and that heat is usually liberated in this case. He also made the very important observation that adsorption occurs the better, the easier a gas is liquefied. At the end of the 19th century, the American physicist G. Gibbs elaborated the general thermodynamic theory of adsorption. In the 20th century, the adsorption phenomenon was thoroughly investigated by I. Langmuir, M. Polanyi, and J. de Boer, and in the Soviet Union, by L. Gurvich, N. Shilov, M. Dubinin, A. Kiselev, and others.

There is *physical* or *van der Waals* adsorption, and *chemical* adsorption or *chemisorption.* In the former case, the adsorption forces have the same nature as intermolecular, or van der Waals, forces. Physical adsorption is always reversible. In chemical adsorption, the adsorption forces have a chemical nature. Chemisorption is usually irreversible. In this textbook, we will consider mainly physi-

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* The adsorbed substance is sometimes called the *adsorbate.* However, this may cause misunderstanding because some scientists use the term "adsorbate" for the adsorbent with the adsorptive adsorbed on it.

cal adsorption and indicate the basic difference between the two types of adsorption only in the appropriate place.

In chemical adsorption, the adsorptive molecules, which are bound to the adsorbent by strong chemical forces, naturally cannot move on the surface of the latter. In contrast, in physical adsorption, there may be both non-localized adsorption when the adsorptive molecules are capable of moving on the surface of the adsorbent, and localized adsorption when the adsorptive molecules are incapable of moving along the surface. Localized physical adsorption is explained by the fact that the adsorbent surface consists of various atoms, ions, or molecules that react with the adsorptive molecules differently. For the adsorptive molecules to move on the adsorbent surface, they must apparently overcome definite potential barriers. However, such barriers often cannot be overcome if they are large enough. Of course, as temperature rises, localized physical adsorption may become non-localized owing to the growth in the kinetic energy of molecules and their ability to overcome the potential barrier.

Physical adsorption occurs spontaneously. The adsorptive tends to occupy the entire adsorbent surface but this is hindered by *desorption*, a process that is the opposite of adsorption and is caused, like diffusion, by the tendency towards uniform distribution of substance particles owing to thermal motion. For every adsorptive concentration, there is a state of adsorption equilibrium, similar to the equilibrium between condensation and evaporation, in the environment. Of course, the higher the adsorptive concentration, the greater is adsorption. It is also clear that the higher the temperature, the smaller is physical adsorption. For every temperature, there is a state of adsorption equilibrium. The effect of temperature on physical adsorption completely obeys the Le Chatelier-Braun principle because desorption, being a process opposite to adsorption, is accompanied with heat uptake.

To determine the amount of the adsorbed substance, it is necessary to experimentally find the gas pressure or the adsorptive concentration in a vessel where adsorption is occurring prior to and after adsorption. The amount of the adsorbed substance is often determined by the gain in weight of the adsorbent. The determination of the amount of an adsorbed substance is often very difficult as a small sought-for quantity is the difference between two large quantities being measured. To reduce the error, determination is usually made by using, as an adsorbent, porous bodies having a large specific area and thus binding a large amount of the adsorptive. However, here the pore diameter of the adsorbent may affect adsorption. Comparatively large molecules of the adsorptive cannot penetrate into the narrow capillaries of the adsorbent, and the adsorption limit attained will be an erroneous quantity which does not charac-

terize the adsorption interaction between the adsorptive and the adsorbent. When the pore diameter is small, the adsorptive may become liquefied (capillary condensation), and the amount of the adsorbed substance will be overestimated.

Quantitatively, adsorption may be expressed by several parameters:

1. By the quantity a, which represents the amount of the adsorptive that is in the volume of the adsorption layer corresponding to unit mass of the adsorbent. This quantity is usually measured in units of mole/g.

2. By the quantity α, which shows the amount of the adsorbed substance per unit surface of the adsorbent. This quantity is merely the surface concentration of the adsorptive. Its units of measurement are mole/m^2 and mmole/cm^2.

3. By Gibbs' quantity Γ, which represents an excess in the number of moles of the adsorptive in the volume of the surface layer having an area of one square centimetre, in comparison with the number of moles of the adsorptive in the same volume, provided a change in the adsorptive concentration did not occur at the interface. When adsorptive concentrations are low, the quantity of Gibbs' adsorption Γ is similar to that of surface concentration α, and at high adsorptive concentrations, the quantity Γ differs from α. When, for some reason, the concentration of the adsorptive in the surface layer is smaller than that in the volume, the quantity Γ is negative, and the phenomenon itself is known as *negative adsorption.*

Adsorption may be characterized by:

(1) the dependence of the amount of the adsorbed substance a on temperature at constant equilibrium pressure p or constant equilibrium concentration c; the graphs $a = f(T)$ at $p = \text{const}$ are known as *isobars*, while at $c = \text{const}$, *isopycnics* of adsorption;

(2) the dependence of equilibrium pressure (or concentration) on temperature at a constant amount of the adsorbed substance; the graphs $p = f(T)$ and $c = f(T)$ at $a = \text{const}$ are known as *isosteres*;

(3) the dependence of the amount of the adsorbed substance a on equilibrium pressure (or concentration) at constant temperature; the graphs $a = f(p)$ or $a = f(c)$ at $T = \text{const}$ are known as adsorption *isotherms.* Isotherms are especially important in the investigation of adsorption, and therefore we will later confine ourselves mainly to a consideration of this dependence. Typical isotherms of adsorption are schematically represented in Fig. 4.1. As we see, isotherms have three parts. The initial, steep and almost straight part of the curve shows that adsorption is practically proportional to pressure or concentration at low values of these parameters. This corresponds considerably to the still free surface of the adsorbent. The almost horizontal part at high values of pressure or concentration corresponds to the adsorbent surface that is completely saturated

with the adsorptive. Under these conditions, if only a monomolecular adsorptive layer can be formed on the adsorbent surface, the amount of the adsorbed substance virtually does not depend on pressure or concentration. The central part of the curve corresponds to the intermediate degrees of adsorption on the surface.

A sharp rise of the isotherm at low equilibrium concentrations is well in keeping with the fact that the remaining quantities of the

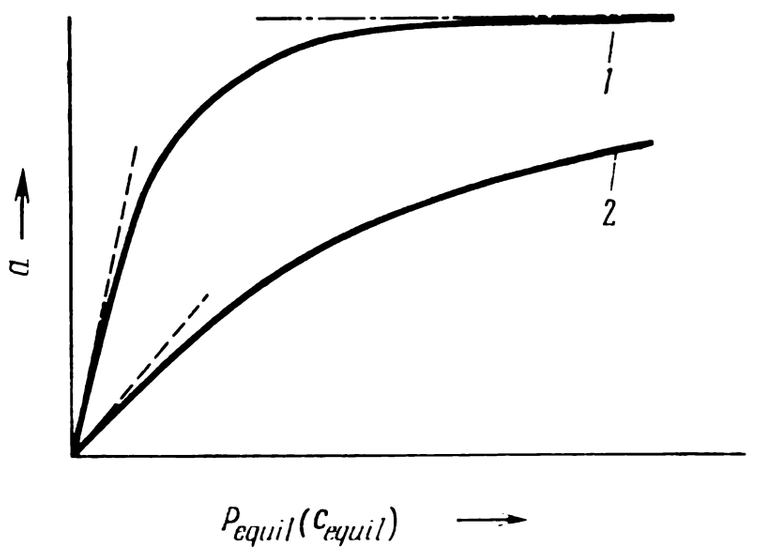


Fig. 4.1. Ordinary shape of adsorption isotherms at different temperatures: *1*—isotherm corresponding to temperature T_1; *2*—isotherm corresponding to temperature T_2 ($T_1 < T_2$)

adsorptive are desorbed from the adsorbent surface with great difficulty. For example, in order to remove traces of gas adsorbed on the inner surface of devices, it is necessary to carry out long evacuation, sometimes at elevated temperature. The ideal isotherm of physical adsorption does not have any sharp inflections which are sometimes characteristic of isotherms of adsorption that is accompanied with chemical interactions. This indicates that no chemical compounds of the adsorbent and the adsorptive are formed in the course of physical adsorption.

It is quite clear from what we have said about the dependence of adsorption on temperature that, as temperature rises, the quantity of equilibrium adsorption decreases and, as a result, isotherms for high temperatures are below the isotherms for low ones (see Fig. 4.1). However, as temperature rises, the *adsorption limit*, i.e., the amount of the adsorptive per unit surface at the closest packing of its molecules in the monomolecular layer, should not change. The adsorption limit is virtually independent of temperature, and should be determined only by the dimensions of the adsorptive molecules. Consequently, isotherms which correspond to different temperatures should have merged together eventually with a rise in equilibrium pressure or concentration. However, this is usually not observed because at

high temperatures the adsorption limit would correspond to very high equilibrium pressure or concentration.

The adsorption isotherm looks like a parabola. Therefore, for its analytical expression, Baedeker and then Freundlich proposed the empirical equation

$$a = x/m = Kp^{1/n} \tag{4.1}$$

where x = amount of the adsorbed substance;
m = mass of the adsorbent;
p = equilibrium gas pressure in a system;
K and $1/n$ = constants.

For adsorption from a solution, Freundlich's equation is as a rule written in the form

$$a = x/m = \beta c_{equil}^{1/n} \tag{4.2}$$

where β = constant which corresponds to constant K of the preceding equation;
c = equilibrium concentration.

Constant β of Eq. (4.2) usually varies within a wide range. Its physical meaning becomes clear if we take $c = 1$; then, β will represent adsorption at the equilibrium concentration of the adsorptive that is equal to 1 mole/l. The exponent $1/n$ in both equations is a proper fraction and characterizes the degree of approximation of an isotherm to a straight line. From what we have said about the change in the shape of an isotherm with temperature, it is easy to see that as temperature rises, the coefficients K and β should decrease while $1/n$ should increase.

The constants of Freundlich's equation may be easily found graphically by the isotherm plotted in logarithmic coordinates. For example, for adsorption from a solution, we have

$$\log a = \log \beta + 1/n \log c_{equil} \tag{4.3}$$

This equation is for a straight line. Taking the logarithms of the experimentally found values of a and c and plotting $\log a$ and $\log c$ on the coordinate axes, we obtain a graph illustrated in Fig. 4.2. The segment cut off by a straight line on the ordinate is equal to $\log \beta$, while the tangent of inclination θ of a straight line to the abscissa is equal to $1/n$. It should be noted that, when the logarithm of Eq. (4.2) is taken, a is expressed in mmole/g while c_{equil}, in mole/l.

Freundlich's equation is an empirical one. In addition, this equation of the parabola cannot explain the almost rectilinear rise in adsorption which does not depend on concentration. Apparently, the almost rectilinear region of an isotherm which corresponds to low pressures or concentrations may be obtained by means of Freundlich's equation only when $1/n = 1$. Likewise, the horizontal rectilin-

ear region of an isotherm which corresponds to high pressures or concentrations may be obtained only at $1/n = 0$. Hence, the exponent $1/n$ should be a function of p or c. Since $1/n$ is taken as constant and as lying in the range of 0.2-1.0 for adsorption from a gaseous

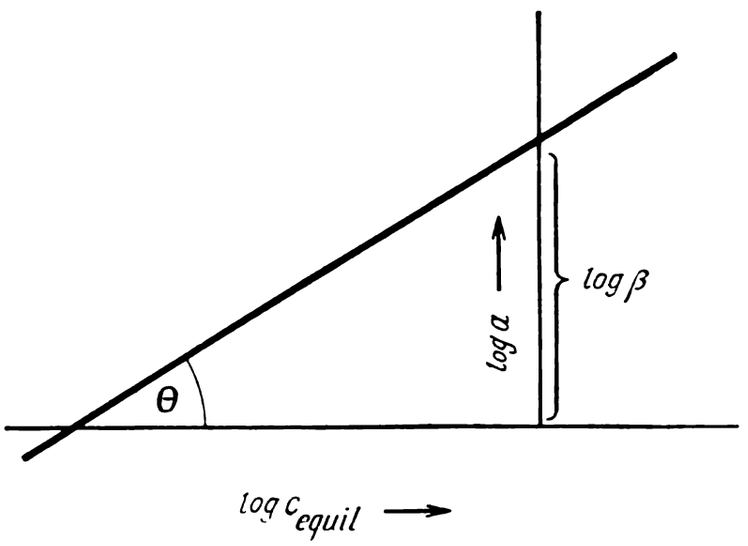


Fig. 4.2. Adsorption isotherm in logarithmic coordinates

medium and in the range of 0.1-0.5 for adsorption from solutions, Freundlich's equation is suitable only for average pressures or concentrations. Analytically, adsorption isotherms on the whole are described far better by the well-known Langmuir equation which is considered in detail further.

2. NATURE OF ADSORPTION FORCES

The adsorptive molecules may interact with the adsorbent surface during physical adsorption owing to different causes. Let us consider these causes briefly since a detailed consideration of adsorption forces is not within the scope of colloid chemistry, and information on them may be found in special monographs on adsorption or in basic textbooks of physical chemistry.

The simplest case is the adsorption of a non-polar molecule by a non-polar adsorbent when only the dispersion forces of attraction and the Born forces of repulsion are in action.

The potential θ which determines the interaction between an adsorbent molecule and an atom of the non-polar adsorptive may be expressed roughly by the Lennard-Jones equation

$$\theta = -Cr^{-6} + Br^{-12} \tag{4.4}$$

where r = distance between particle centres;

C = constant which characterizes the energy of dispersion attraction;

B = constant which characterizes the energy of repulsive forces.

The constant C for atoms with many electrons may be expressed with the aid of equations describing electric and magnetic properties of interacting molecules and based on concepts of quantum mechanics which will not be considered here. An important fact is that, as is shown in textbooks of physical chemistry, the energies of not only dispersion forces, but also induction and orientation forces of attraction, depend on distance r in the same manner, i.e., they are inversely proportional to the sixth power of the distance.

The expression Br^{-12} is introduced into Eq. (4.4) as a good empirical approximation. It is quite obvious that attractive forces should prevail at comparatively large distances, and repulsive forces, at very small ones. It is also clear that these forces must be equal at a definite distance because this corresponds to the minimum of the free energy of a system.

However, since in adsorption the dispersion forces act simultaneously between each non-polar particle, say argon atoms, and all the adjacent adsorbent atoms, the total potential Φ of the adsorption forces may be obtained roughly by summing up the potential of pairwise interactions of the argon atom with every atom of the adsorbent, taking account of the potential of the repulsive forces:

$$\Phi = \sum_i \theta_i = -C \sum r_i^{-6} + B \sum r_i^{-12} \qquad (4.5)$$

In this equation, $-C \sum r_i^{-6}$ is the total potential of the dispersion forces of attraction, $B \sum r_i^{-12}$ is the total potential of the repulsive forces, and r_i is the distance from the centre of the argon atom to centres of adsorbent atoms. Since the interaction energy of particles rapidly decreases with the distance, it is practically enough to sum up with 100-200 adjacent adsorbent atoms. An important fact is that in the adsorption of complex non-polar molecules, the potential energy of interaction may be roughly calculated as the sum of the potential energies of adsorption of its units (force centres).

If the adsorbent consists of ions instead of atoms, besides the action of dispersion forces, there is the action of induction forces of attraction of a dipole induced in the adsorptive molecule by the electric field created by ions of the adsorbent lattice. Here, the share of induction forces in an adsorption interaction is proportional to the polarizability of the adsorptive molecule and to the square of the intensity of the electrostatic field above the adsorbent surface.

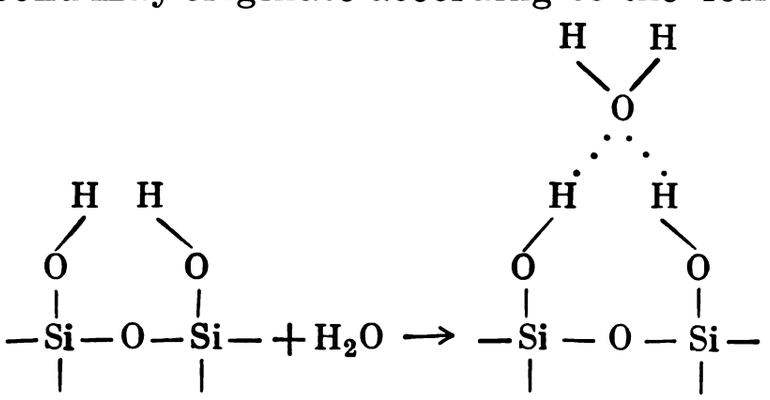
If polar molecules are adsorbed on the non-polar adsorbent, the constant dipoles of adsorptive molecules polarize adsorbent atoms, i.e., induce electric moments in them. As a result, induction attraction originates, and it is added to dispersion attraction. Induction interaction is usually not great and may attain several kcal/mole at the most, depending on the dipole moment of the adsorptive molecule and the polarizability of the adsorbent.

Lastly, if polar molecules are adsorbed on the adsorbent which has ions or dipoles on its surface, the ions or dipoles of the adsorptive begin to interact with the electrostatic field of the adsorbent. In this case, adsorptive molecules may orient in the electrostatic field of the adsorbent, i.e., orientational Coulomb interaction occurs.

It should be noted that, while the total dispersion interaction of the adsorptive molecule with the adsorbent is always greater than its interaction with one active adsorbent centre, the total electrostatic interaction of the adsorptive molecule may also be smaller than its electrostatic interaction with one adsorbent centre. This may be explained by the fact that the negative pole of the adsorptive molecule dipole is attracted by the cation of the adsorbent lattice and, at the same time, is repulsed by anions which are adjacent to the cation and form with cations an adsorbent surface of alternating signs.

The energies of induction interaction and of orientational interaction are usually far smaller than the energy of dispersion interaction; therefore, it is often assumed that the energy of intermolecular attraction is determined by the energy of dispersion attraction.

Adsorption which is similar to physical adsorption may be also caused by the formation of hydrogen bonds. In particular, this bond originates when molecules are adsorbed on surfaces having hydroxyl groups of water, alcohols, ammonia, or amines. For example, when water is adsorbed on the hydroxylated surface of a silica gel, the hydrogen bond may originate according to the following pattern:



When the hydrogen bond is being formed, the energy of interaction between the adsorptive and the adsorbent is rather high; therefore, the heat dissipated upon such adsorption is usually considerably greater than that in the case of adsorption of substances which are similar by their geometric shape and dimensions but do not form hydrogen bonds.

A considerable contribution to the elucidation of adsorption phenomena was made by infrared spectroscopy. In particular, A. Terenin showed that hydroxyl groups are perturbed when being adsorbed on the silica surface; the infrared spectrum shows a shift in the frequency of stretching vibrations of the surface hydroxyl groups towards greater wavelengths. This shift is different for various molecules adsorbed on the surface.

3. LANGMUIR'S MONOMOLECULAR ADSORPTION THEORY

There is the adsorption of a gas on a solid, the adsorption of a solute at the gas—solution interface, and the adsorption of a solute at the solid—solution interface.

The adsorption of a gas on a solid is the simplest case of adsorption, because the gas—solid system consists of only two components. Therefore, the adsorption of a gas by a solid is especially convenient for theoretically considering adsorption phenomena.

There are several theories of physical adsorption, among which we will first of all consider the **monomolecular adsorption** theory. It was proposed in 1915 by the American scientist I. Langmuir but, as he himself noted, he used the concepts of adsorption forces that were first put forward by the Russian scientist L. Gurvich.

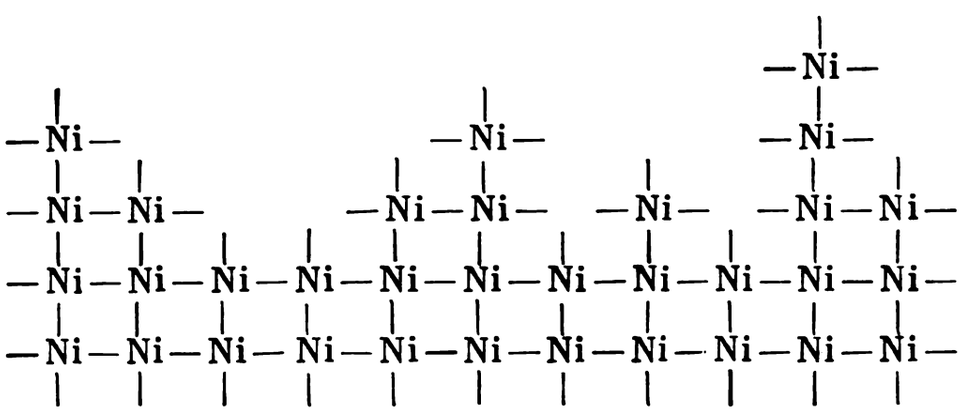
Langmuir proceeded from the following principles when he was elaborating his theory:

1. Adsorption is localized and is caused by forces which are similar to chemical ones. However, according to Langmuir, chemical forces are all those which are involved in the cohesive strength of a substance, evaporation, crystallization, surface tension, and so forth.

2. Molecules are adsorbed on active centres which are always present on the adsorbent surface. Such centres may be peaks and elevations which exist on any, even the smoothest, surface. For example, the surface of calc-spar crystals has projections to a height of 10^{-4}-10^{-5} cm; even finely polished mirrors have projections to a height of 3×10^{-7} cm on their surface.

Owing to the great unsaturation of the force field near such peaks and elevations, these regions are capable of retaining gas molecules which flow on them, and the less saturated the adsorbent molecules on the surface of the centre, the more active is the centre.

An example of a surface having centres of different activity is that of reduced nickel, for which Taylor gives the following structure pattern



Owing to great unsaturation, nickel atoms connected with the surface layer by a single bond adsorb molecules more firmly or in a greater amount than those connected with the surface by two bonds and, especially, by three and more bonds.

Several researchers also hold that active centres are edges and corners of crystals and the boundaries of grains in the microheterogeneous adsorbent near which especially intensive force fields are formed. The fact that edges and corners of crystals have great ability to adsorb molecules may be seen from the following example: if a copper sulphate crystal is put into an alcohol solution of hydrogen sulphide, the crystal begins to blacken, as a result of the formation of copper sulphide, always from corners and edges.

It is usually assumed that active centres occupy only a small part of the adsorbent surface. This viewpoint is confirmed by the fact that the amount of substance which poisons a catalyst is as a rule far less than that required for covering the entire adsorption surface with it.

3. Owing to the small radius of action of adsorption forces which have an almost chemical nature, and to their saturability, every active centre, while adsorbing the molecule, becomes incapable of further adsorption. As a result, only a monomolecular adsorptive layer may be formed on the adsorbent surface.

4. Adsorbed molecules are retained by active centres only for a definite length of time. After a lapse of time, as a result of fluctuation of the kinetic energy, molecules tear away from the adsorbent surface and pass over to the gaseous phase. Then, active centres may adsorb new molecules which in turn are desorbed, and so forth.

The time of stay of a molecule in the adsorbed state in the active centre largely depends on temperature. At low temperatures, the time may be very great. At high temperatures in the range of 1000-2000 °C, the time of stay of a molecule in the adsorbed state may be only millionths of a second.

5. Langmuir took no account of the forces of interaction between adsorbed molecules. In other words, according to Langmuir, the time of stay of gas molecules in active centres does not depend on whether the neighbouring active centres are occupied by gas molecules or not.

Proceeding from the foregoing principles, Langmuir presented a general equation for the isotherm of localized adsorption that was suitable for describing the adsorption of both gases and solutes.

To derive this equation with respect to gas adsorption, let us suppose that localized adsorption is a quasichemical reaction between a gas molecule and an adsorbent active centre as a result of which an adsorption complex, i.e., a molecule adsorbed by the adsorbent, is formed:

$$\text{gas molecule} + \text{adsorbent active centre} \rightleftarrows \text{adsorption complex}$$

According to this reaction and taking into account that the number of collisions between gas molecules and the adsorbent surface is proportional to gas pressure, we may write

$$\alpha = kp\alpha_0 \tag{4.6}$$

where α = surface concentration of the adsorptive;
α_0 = concentration of free active centres on the adsorbent surface;
p = gas pressure;
k = constant which does not depend on concentration and is invariable at a given temperature.

In the steady-state adsorption equilibrium

$$k = \alpha/(p\alpha_0)$$

In this case, k is the equilibrium constant.

Taking into account that every active centre can be occupied by one molecule, we may write

$$\alpha + \alpha_0 = \alpha_{max} \tag{4.7}$$

where α_{max} = surface concentration of the adsorptive bound to all the active centres.

Eq. (4.7) may be rewritten as

$$\alpha_0 = \alpha_{max} - \alpha \tag{4.8}$$

Substituting this equation in Eq. (4.6), we have

$$\alpha = kp\,(\alpha_{max} - \alpha) \tag{4.9}$$

Solving Eq. (4.9) with respect to α, we obtain

$$\alpha = \alpha_{max}kp/(1 + kp) \tag{4.10}$$

This is Langmuir's adsorption isotherm equation. It is sometimes written in a somewhat different way

$$\alpha = \frac{\alpha_{max}p}{1/k + p} = \frac{\alpha_{max}p}{A + p}$$

where A = quantity which is inverse to the equilibrium constant.

Since the quantity of adsorption a is proportional to α, Langmuir's equation may be represented

$$a = a_{max}kp/(1 + kp) = a_{max}p/(A + p) \tag{4.11}$$

In this equation, a_{max} is the amount of the adsorptive (in moles) that is adsorbed per unit mass of the adsorbent (one gram) which corresponds to the complete filling up of all the active centres. Hence, in Langmuir's equation, both constants α_{max} (or a_{max}) and k have a definite physical meaning.

Langmuir's equation, unlike Freundlich's, gives a good description of the adsorption isotherm, producing almost rectilinear regions on the graph at low and high values of p.

Indeed, at low pressures, the term kp in the denominator of Eq. (4.11) which is very small in comparison with unity can be neglected, and Langmuir's equation will become identical to Henry's equation for the distribution of a substance between two phases: $a = a_{max}\,kp = Kp$. Hence, at low values of p, the adsorbed amount

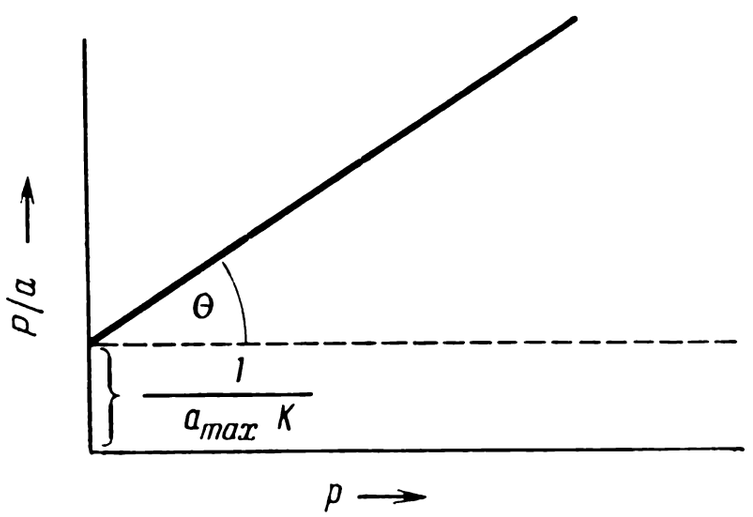


Fig. 4.3. Solution of Langmuir's equation by its transformation into a straight-line equation

of a substance is directly proportional to equilibrium pressure. This case corresponds to the initial, almost rectilinear, region of the isotherm. At high values of p, conversely, unity in the denominator of Langmuir's equation can be neglected, and then the equation will have the form of $a = a_{max}$, i.e., the adsorbed amount of a substance does not depend on pressure, and this corresponds to the relatively rectilinear region of the isotherm that is almost parallel to the pressure axis.

For the graphic solution, Langmuir's equation is reduced to the form:

$$\frac{p}{a} = \frac{1}{a_{max}k} + \frac{p}{a_{max}} \qquad (4.12)$$

The equation obtained is the equation of a straight line in the coordinates of p/a and p. This is seen in Fig. 4.3. Apparently, $a_{max} = \cot\theta$ where θ is the angle of inclination of a straight line to the abscissa, and $1/(a_{max}k)$ is the segment cut off by a straight line on the ordinate axis. Knowing $1/(a_{max}k)$ and a_{max}, it is easy to calculate k*.

* Another, albeit somewhat less precise, technique of graphically solving Langmuir's equation may be found in the first Russian edition of this textbook, *Kurs kolloidnoi khimii* by S. S. Voyutsky, Moscow, Khimiya, 1964, p. 110.

As we know, k, the equilibrium constant of any chemical reaction, is connected with Q, the heat of reaction, by the equation

$$k = ge^{Q/RT} \tag{4.13}$$

where g = constant factor.

Since heat is always dissipated in physical adsorption, i.e., $Q > 0$, it follows from Eq. (4.13) that the equilibrium constant should decrease with an elevation of temperature. This occurs owing to an increase in the kinetic energy of molecules and the consequent growth

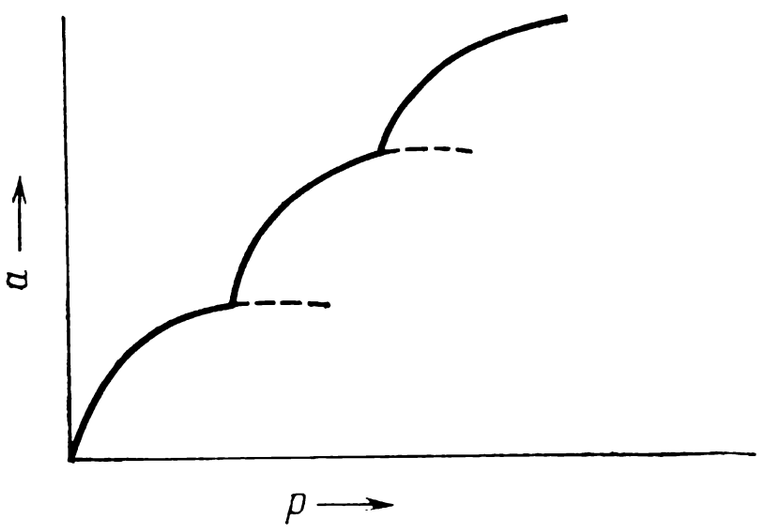


Fig. 4.4. Isotherm of stepwise adsorption

of desorption. Hence, it is clear why gas adsorption is inconsiderable at high temperatures and at a pressure which is not too high, and why the adsorption limit is not attained under these conditions (see Fig. 4.1).

Langmuir's adsorption isotherm equation is well applicable if adsorption is caused by forces which are similar to chemical forces by their nature, and if adsorption is not complicated by several secondary phenomena, such as the dissociation of molecules of adsorbed gas on the surface.

Concepts elaborated by Langmuir make it possible to explain **stepwise adsorption.** In this case, the adsorption isotherm has a specific stepwise shape, as is shown in Fig. 4.4. This phenomenon may be easily explained if it is assumed that the adsorbent surface has groups of active centres which greatly differ from one another by their activity. The first step of the isotherm apparently corresponds to the filling up of a group of the most active centres which occurs already at low pressures; the second, to the filling up of a group of active centres having lower activity, and this requires higher pressure; and so forth.

However, some cases of physical adsorption cannot be explained by the theory of monomolecular adsorption, they require a fundamentally different approach from the standpoint of polymolecular adsorption.

4. POLANYI'S POLYMOLECULAR ADSORPTION THEORY AND THE BET (BRUNAUER, EMMETT, AND TELLER) THEORY

As has been shown by experiments, together with adsorption isotherms whose shape is given in Fig. 4.1, isotherms which do not have the second region that is almost parallel to the pressure axis and that corresponds to the saturation of the adsorbent surface by the adsorptive molecules are found rather often in practice. The shape of such isotherms is given in Fig. 4.5. As we see, Langmuir's

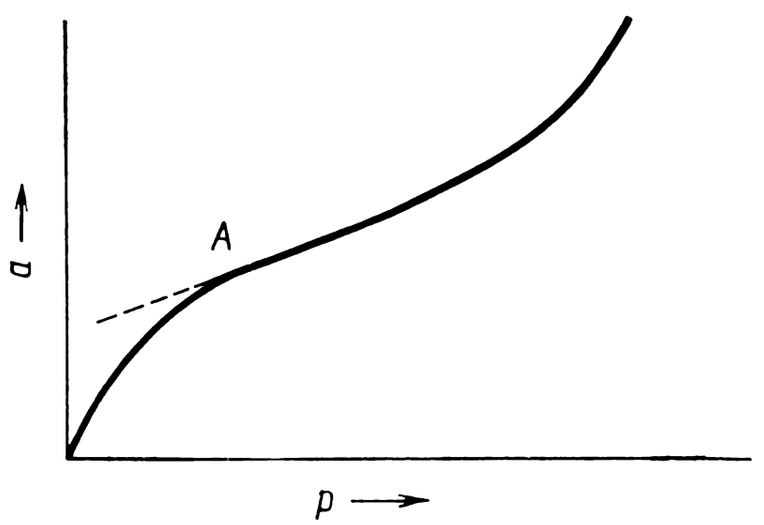


Fig. 4.5. Isotherm of polymolecular adsorption

isotherm sharply rises at point A. Apparently, the adsorptive continues to be bound by the adsorbent after the formation of the monomolecular layer. The shape of such isotherms cannot be explained as the outcome of capillary condensation because they are observed also for non-porous adsorbents when capillary condensation is impossible.

To explain this phenomenon, Polanyi in 1915 proposed the theory of **polymolecular adsorption** which is also called the **potential** theory. Let us briefly consider the basic principles of this theory which is especially suitable for the adsorption of vapours on a solid.

1. Adsorption is caused by purely physical forces.

2. The adsorbent surface does not have any active centres while the adsorption forces act in the vicinity of the adsorbent surface and form near it a continuous force field from the side of the gaseous phase.

3. Adsorption forces act at comparatively great distances, in any case at distances which are greater than the dimensions of adsorptive molecules, and therefore we may say that the adsorbent surface has an *adsorption volume* which is filled with adsorptive molecules during adsorption.

4. The action of adsorption forces decreases with the distance from the surface, and at a certain distance practically becomes null.

5. The attraction of a given molecule by the adsorbent surface does not depend on the presence of other molecules in adsorption space, and therefore polymolecular adsorption is possible.

6. Adsorption forces do not depend on temperature and consequently the adsorption volume does not change with temperature. This does not contradict the fact that adsorption diminishes as

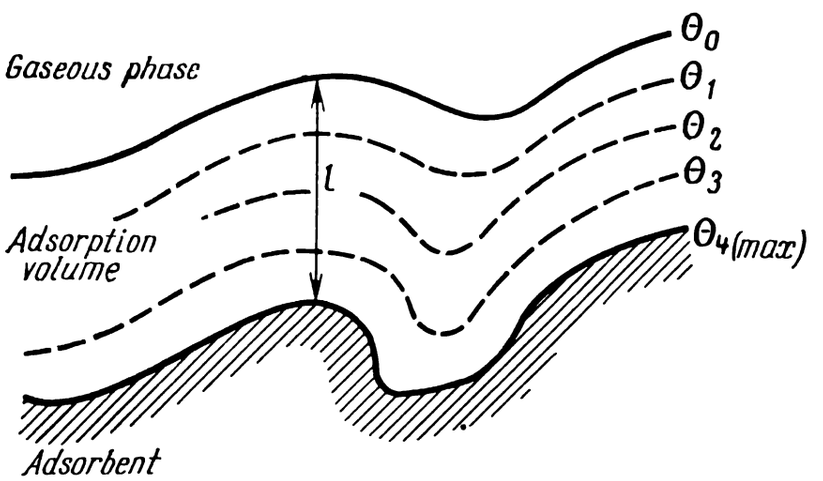


Fig. 4.6. Diagram of the adsorption volume according to the polymolecular theory of adsorption

temperature rises; this is caused not by a decrease in adsorption forces, but by an increase in the intensity of thermal motion of adsorbed molecules as a result of heating and hence in the rate of desorption.

From our consideration of the principles of the polymolecular adsorption theory, we may see that the force field which originates at the adsorbent surface is in many respects similar to the gravitational field: the non-saturability of the field by the adsorptive molecules which are directly on the adsorbent surface; the independence of forces acting in the field of temperature.

Figure 4.6 schematically shows a section of the adsorption volume that is in accordance with the polymolecular adsorption theory. Equipotential surfaces, i.e., surfaces with the same adsorption potential, may be imagined in the adsorption field, like in any force field. In the figure, they are denoted by dotted lines. The adsorption potential θ implies work done against the adsorption forces when one mole of the adsorptive (vapour) is displaced from a given point of the field to the gaseous phase. Apparently, the maximum adsorption potential should exist at the interface between the adsorbent and adsorption volume. The potential θ should be null at the interface between the adsorption volume and gaseous phase, i.e., at the place where the action of adsorption forces ceases.

In the polymolecular adsorption theory, a change in the adsorption potential is usually expressed not as a function of distance l

from the adsorbent surface but as a function of the adsorption volume V, because the function $\theta = f(V)$ is determined experimentally rather easily while unsurmountable difficulties are sometimes encountered when the function $\theta = f(l)$ is being found. Indeed, it is easy to find the adsorption volume if work is carried out, for example, at sufficiently low temperatures. The adsorptive is then in adsorption space as a liquid. In this case, V_{liq}, the adsorption volume filled up by a liquid and corresponding to one gram of the adsorbent, is expressed by the equation

$$V_{liq} = aV_{mol} \tag{4.14}$$

where a = amount of the adsorptive (in moles) which is adsorbed by one gram of the adsorbent;
V_{mol} = molar volume of the condensate.

The thickness of the liquid layer in the adsorption volume may be found by the equation

$$l_{liq} = V_{liq}/s \tag{4.15}$$

where s = adsorbent surface area.

Unfortunately, owing to the difficulty in determining the true surface area of the adsorbent, it is often difficult to determine this quantity, and therefore Polanyi proposed to express θ not as a function of l but as a function which is proportional to the quantity V.

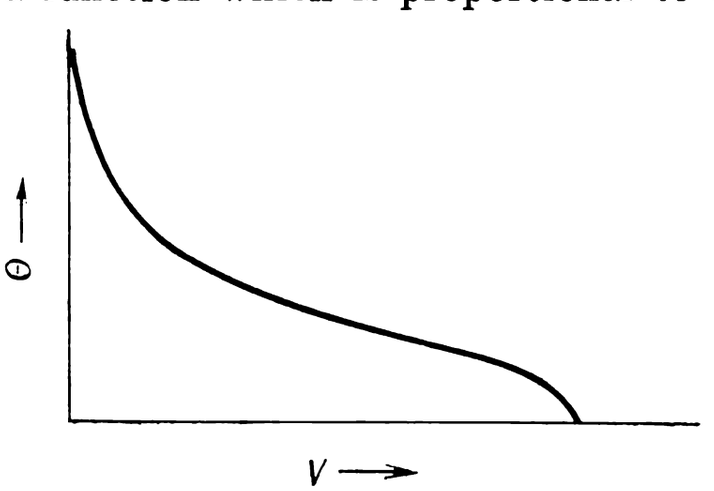


Fig. 4.7. Typical shape of the characteristic curve

Figure 4.7 shows a change in the adsorption potential θ with a change in the adsorption volume V as Polanyi imagined it. Such curves which do not depend on temperature and are characteristic of every given adsorbent were called *characteristic curves* by Polanyi.

According to the polymolecular adsorption theory, the equation of the gas state is applicable to the adsorption volume. Therefore, the isotherms which characterize the dependence of the adsorptive density ρ on the adsorption volume V for various temperatures are similar to the isotherms of p, V.

Under definite conditions, say at a sufficiently low temperature, the adsorption forces on the surface may cause the condensation of a vapour to a liquid having a density of ρ_{liq}. At temperatures which are considerably lower than the critical temperature, the entire adsorption volume will be filled with liquid as a result of condensation, and therefore $V_{liq} = V_{max}$. In this case, the curve $\rho = f(V)$ in the region which corresponds to the adsorption volume is almost parallel to the abscissa owing to the low compressibility of liquid. Later, the curve sharply drops at the adsorption volume—gaseous phase interface, and adsorptive density attains the value of density of the gaseous phase ρ_0.

At temperatures which are considerably higher than the critical temperature, the adsorptive will act as an ideal gas, and the graph of dependence of ρ on V is expressed by a curve similar to the isotherm for ideal gas $pV = RT$. In this case, the adsorbed gas will have maximum density on the adsorbent surface, and minimum density in the immediate vicinity of the gaseous phase. Here, adsorptive density in the adsorption volume does not reach liquid density at any place.

Lastly, when temperature is close to the critical temperature, the dependence of ρ on V is apparently expressed by a curve whose shape is similar to that of the isotherm described by the van der Waals equation. In this case, part of the adsorbed substance will be in the adsorption volume in the liquid state, and the other part, in the gaseous state. Therefore, the curve drops most sharply in the region which corresponds to the transition of a liquid to a gas.

Proceeding from the foregoing concepts, Polanyi showed how to plot the characteristic curve. The potential θ_i which conforms to point i that is at the liquid—gas interface in the adsorption volume may be represented as the work of compression of one mole of gas at temperature T

$$\theta_i = \int_{p_0}^{p_i} V\,dp \tag{4.16}$$

where p_i = pressure of saturated vapour over the liquid surface;
p_0 = gas pressure in the gaseous phase.

Since $V = RT/p$, the value of θ_i can be calculated by the equation

$$\theta_i = \int_{p_0}^{p_i} V\,dp = RT \int_{p_0}^{p_i} \frac{dp}{p} = RT \ln \frac{p_i}{p_0} \tag{4.17}$$

The value of p_i for most substances is known; the value of p_0 is determined experimentally. To plot the respective point on a diagram that expresses the dependence of the adsorption potential

on the adsorption volume, it is necessary to know the value of V_i to which the value of θ_i conforms. To this end, Eq. (4.14) is used.

The graph $\theta = f(V)$ may be plotted after determining V_i and θ_i for several values of p_0 at a temperature which is considerably lower than the critical one when the adsorptive is in the adsorption volume mainly as a liquid. The presence of the factor T in the right-hand member of Eq. (4.17) does not indicate that the dependence of θ_i on V_i should change with temperature; it only shows that at another temperature, but at the same value of p_0, the adsorption potential which corresponds to the liquid—gas interface will be different.

M. Dubinin showed that the potential theory of adsorption makes it possible to calculate the isotherm of adsorption of various vapours on the same adsorbent according to the characteristic curve obtained from the isotherms of adsorption of a single vapour because the relationship of adsorption potentials of various vapours is almost independent of the adsorption volume. It follows that the coordinates of the points of characteristic curves for different adsorptives, in the case of the same adsorbent, at all values of the adsorption volume are in constant relation β, i.e., these curves are affined. The relation β is known as the *affinity coefficient* of characteristic curves. It follows that, when the characteristic curve is plotted according to the experimental isotherm of adsorption of an adsorptive, and the respective affinity coefficient of another adsorptive is known, the adsorption isotherm for the second adsorptive can be found.

We have briefly considered two adsorption theories, i.e., Langmuir's monomolecular adsorption theory and Polanyi's polymolecular adsorption theory, which at first seem to be mutually exclusive. Which of them is more correct? The answer is that both theories are limited in their application. Sometimes one theory is applicable, and at other times, the other, depending on the nature of the adsorbent and that of the adsorptive, and especially on the conditions of adsorption. Polanyi's theory is applicable only to phenomena of purely physical adsorption. Langmuir's theory covers, though with certain limitations, the phenomena of both physical and chemical adsorption. However, Langmuir's theory cannot be used to explain adsorption of fine-pored adsorbents which have narrowing pores. Owing to the additivity of the dispersion forces, the adsorption potential is higher in narrow spaces, and adsorption is more intensive in such places. This is especially noticeable at temperatures below the critical temperature of the adsorptive, i.e., in the adsorption of vapours which in this case fill up the narrowest spaces of capillaries in the form of a liquid. It is difficult therefore to apply Langmuir's equation to adsorption by fine-pored adsorbents which have pores with narrow spaces. Of course, Langmuir's equation may be used to formally describe adsorption by such adsorbents. However, the constant a_{max} in this case does not express capacity of a dense monolayer,

and correct results will no longer be obtained by using this constant for determining the specific surface of such adsorbents.

Attempts were made to generalize Langmuir's and Polanyi's concepts and describe the isotherms of different shapes by a single equation. In particular, such a generalized theory was evolved by Brunauer, Emmett, and Teller in 1935-1940 in respect to the adsorption of vapours. The theory has become known as the BET theory according to the initial letters of the authors' names. The basic principles of the BET theory are given below:

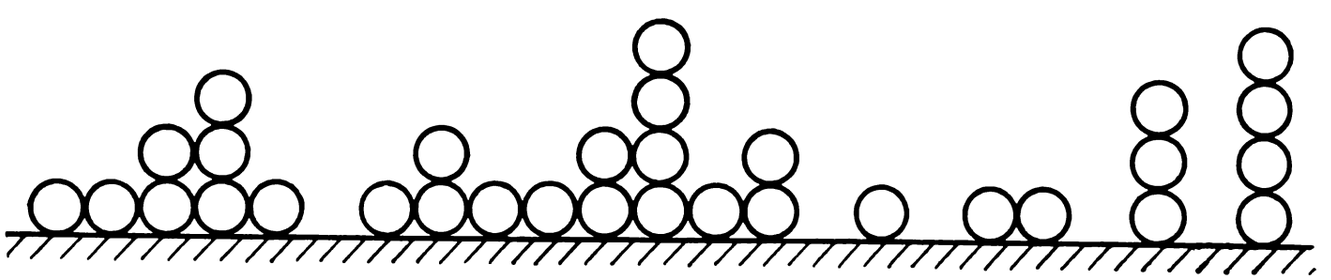


Fig. 4.8. Diagram of polymolecular adsorption according to the BET theory

1. The adsorbent surface has a definite number of active centres which are equivalent energetically and are capable of retaining the adsorptive molecules.

2. For simplicity's sake, the interaction of the neighbouring adsorbed molecules in the first and subsequent layers is neglected.

Both of these allowances correspond to Langmuir's adsorption on a homogeneous surface without the interaction of adsorbed molecules.

3. Each molecule of the first layer is a possible centre for adsorption and the formation of a second adsorbed layer; each molecule of the second layer is a possible centre for adsorption in the third, and so forth.

4. It is assumed that all the molecules in the second and subsequent layers have the same partition function as in the liquid state (which differs from the partition function of the first layer).

Hence, the adsorbed phase may be represented as an ensemble of adsorption complexes, i.e., molecular chains which are started by the molecules of the first layer that are directly connected with the adsorbent surface. No energy exchange occurs between the chains. The structure of the adsorption layer according to the BET theory is schematically illustrated in Fig. 4.8.

All these prerequisites are rather conditional. In particular, according to the BET theory, it is assumed that every molecule of a liquid has only two close neighbours (i.e., from the top and from the bottom in a chain) while the molecule of a real liquid is surrounded with much more adjacent molecules. Nevertheless, the theory turned out to be very useful in some respects.

Polanyi's theory does not make it possible to derive the adsorption isotherm equation. The BET theory, like Langmuir's theory, gives an analytical equation for the isotherm which in this case is S-shaped (see Fig. 4.5). Instead of presenting a rather complex derivation of the adsorption isotherm equation worked out by Brunauer, Emmett and Teller, let us consider only some principles underlying this derivation, and then give the isotherm equation itself.

In deriving the equation, Brunauer, Emmett, and Teller regarded the adsorption of vapour molecules as a series of quasichemical reactions yielding single and multiple adsorption complexes:

$$\text{vapour} + \text{free surface} \rightleftarrows \text{single complexes}$$
$$\text{vapour} + \text{single complexes} \rightleftarrows \text{double complexes}$$
$$\text{vapour} + \text{double complexes} \rightleftarrows \text{triple complexes, and so forth}$$

In this case, Q_1, the heat of adsorption of the first molecular layer, i.e., the heat of formation of single complexes, is much greater than that of all the subsequent layers. The heats of adsorption of all the subsequent layers are approximately the same and are equal to the heat of condensation L.

For C, the equilibrium constant of polymolecular adsorption, we may write

$$C = g' \exp\left(\frac{Q_1 - L}{RT}\right) \tag{4.18}$$

$(Q_1 - L)$ = the so-called *pure heat of adsorption.*

Proceeding from these concepts, Brunauer, Emmett, and Teller derived the following equations for the vapour adsorption isotherm:

$$\alpha = \frac{\alpha_{max} C p/p_s}{(1 - p/p_s)\,[1 + (C-1)\,p/p_s]} \tag{4.19}$$

$$a = \frac{a_{max} C p/p_s}{(1 - p/p_s)\,[1 + (C-1)\,p/p_s]} \tag{4.20}$$

where p_s = pressure of saturated vapour at a given temperature;

p/p_s = relative vapour pressure;

α, α_{max}, a, a_{max}, p have the same meanings as in Langmuir's equation.

At values of p which are far from p_s and $C \gg 1$, adsorption leads to the formation of a monomolecular layer, and Eqs. (4.19) and (4.20) become Langmuir's adsorption equations (4.10) and (4.11). As p approaches p_s, the number of free active centres decreases and the multiplicity of complexes increases. At $p = p_s$, the condensation of vapour occurs.

The BET equation for the polymolecular adsorption isotherm may be easily reduced to a linear one

$$\frac{p/p_s}{a\,(1-p/p_s)} = \frac{1}{a_{max}C} + \frac{C-1}{a_{max}C} \cdot p/p_s \qquad (4.21)$$

The values of the constants a_{max} and C may be found by the inclination of this line and the segment which it cuts off on the ordinate.

The BET theory, like Langmuir's theory, indicates the way of determining the specific area of an adsorbent. When a_{max} is found for vapours of simple substances (N_2, Ar, Kr) at low temperatures and when the area s_0 occupied by an adsorptive molecule is known, it is easy to calculate s_{sp}

$$s_{sp} = a_{max}N_A s_0 \qquad (4.22)$$

where s_{sp} = specific area of the adsorbent;
N_A = Avogadro number.

It is easy to solve also an inverse problem. To this end, the surface s_{sp} of a given adsorbent is determined by measuring the adsorption of standard vapour at low temperatures; then, after experimentally finding the vapour adsorption isotherm for the test adsorptive and the value of the capacity of the monolayer a_{max}, the value of s_0 is calculated:

$$s_0 = s_{sp}/(a_{max}N_A) \qquad (4.23)$$

Determinations of the specific area of the same adsorbent which adsorbs various vapours have produced similar results that in general coincide with those of the determination of the specific area by other, non-adsorption, methods. This confirms the interpretation of the isotherm shape by the BET theory. Notwithstanding several shortcomings, the BET theory is so far the best and most useful theory of physical adsorption.

5. CAPILLARY CONDENSATION

As we have already seen, polymolecular adsorption is characterized by an S-shaped adsorption isotherm which is represented in Fig. 4.5. However, it should be borne in mind that the curve of a similar shape may be obtained in adsorption that is complicated by *capillary condensation*. Let us consider this phenomenon in greater detail.

Capillary condensation is caused by the presence of fine pores in the adsorbent. Adsorptive vapours condense in such pores at pressures which are less than the pressure of saturated vapour over the plane surface because concave menisci are formed in capillaries as a result of merging liquid layers formed on capillary walls owing

to vapour adsorption. Of course, concave menisci may originate only if the liquid formed wets capillary walls.

The connection between radius r of a spherical meniscus which is formed in a capillary put into a liquid that wets its walls, and the pressure p of saturated vapour over the meniscus is given by Thomson's (Kelvin's) well-known equation whose derivation is presented in the textbooks of physics:

$$p = p_s \exp\left(-\frac{2\sigma V_{mol}}{rRT}\right) \tag{4.24}$$

where p_s = pressure of saturated vapour over the plane surface of a liquid;
σ = surface tension of a liquid;
V_{mol} = molar volume of a liquid;
R = gas constant;
T = absolute temperature.

It should be noted that Eq. (4.24) is derived for a concave spherical meniscus. For a cylindrical meniscus, one of whose main values of curvature is null, the equation assumes the following form:

$$p_{cyl} = p_s \exp\left(-\frac{\sigma V_{mol}}{rRT}\right) \tag{4.25}$$

Hence, vapour pressure over a cylindrical meniscus is greater than that over a spherical one in a capillary of the same radius, i.e., $p_{cyl} > p$. This circumstance plays an important role in capillary condensation.

Thomson's equation is the main equation for calculations connected with the phenomena of capillary condensation. If p_s, the vapour pressure of a liquid, and R, the radius of an adsorbent capillary*, are known, the equation may be used to calculate vapour pressure p_h above which condensation begins in capillaries. If p_s and p_h are given, the equation may be used to calculate the maximum radius of capillaries in which condensation will occur (this must be known in order to correctly select the adsorbent).

The condensation phenomenon should not be confused with physical adsorption. The elementary theory of capillary condensation does not take account of the specific action of surface forces. Capillary condensation differs from polymolecular physical adsorption also by the fact that the latter may occur on plane surfaces while capillary condensation cannot.

B. Deryagin and Z. Zorin studied the mechanism of capillary condensation by the optical method on a smooth glass surface. They

* Capillary radius R, as it follows from molecular physics, is connected with r, the radius of curvature of a spherical meniscus of a liquid which wets capillary walls, by the simple equation $R = r \cos\theta$ where θ is the contact angle.

have shown that a steep rise of the isotherm which characterizes capillary condensation begins for non-polar substances (CCl_4 and others) at p/p_s of about 0.98, and for polar substances (water, alcohols, nitrobenzene), at somewhat smaller relative pressures. These scientists also discovered that, when polar substances are being sorbed, there is a sharp transition from the adsorption layer to a liquid phase. This conclusion suggests coexistence of lens-shaped nuclei, i.e., regions of a new liquid phase, and polymolecular adsorption layers of uniform thickness. The liquid phase is formed owing to the growth of these islands while the adsorption layer which surrounds them does not change noticeably. Conversely, the liquid phase in the surface condensation of non-polar substances is formed apparently as a result of the continuous thickening of the adsorption layer; this condensation is reversible.

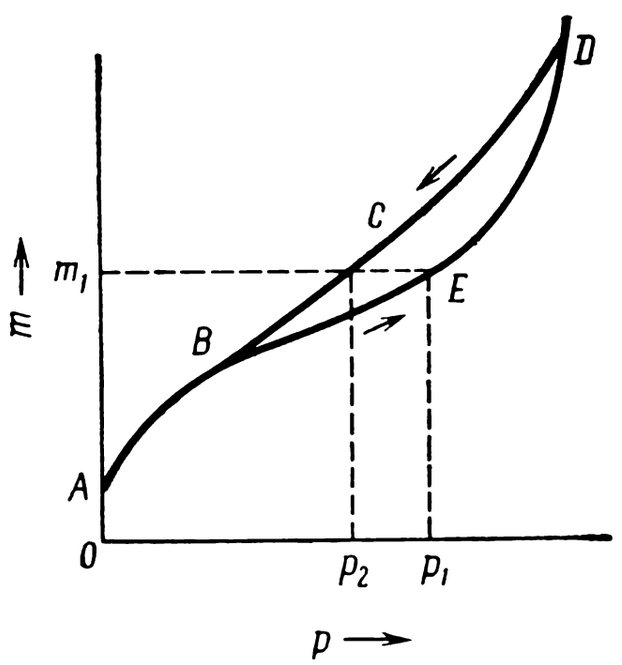


Fig. 4.9. Hysteresis in capillary condensation

Therefore, for polar substances, the difference between the adsorption polymolecular layer and the volume of liquid has the nature of phase distinctions, and polymolecular adsorption layers can be regarded as boundary phases. Conversely, the adsorption layer of vapours of non-polar substances cannot be regarded as a special phase which differs from the liquid phase because a continuous transition can exist between them and their coexistence is impossible.

In adsorption accompanied by capillary condensation, hysteresis is often observed when adsorption and desorption isotherms do not coincide. This phenomenon was studied in detail by van Bemmelen and Zsigmondy for the adsorption of water by silica gel. The results of their experiments are presented schematically as a diagram in Fig. 4.9 where m, the mass of water adsorbed by silica gel, is plotted on the ordinate, and the equilibrium values of vapour pressure p, on the abscissa.

At $p = 0$, silica gel still contains a small amount of water, and this is characterized by the OA segment. This is the water of crystallization which may be removed only by calcination. The adsorption isotherm is reversible only in the AB region. From point B, the isotherm becomes irreversible, i.e., vapour pressure p_1 corresponds to the mass of moisture m_1 in adsorption while p_2 corresponds to the same mass in dehydration, and $p_1 > p_2$. This becomes clear when

a line which is parallel to the abscissa and which intersects the hysteresis loop is plotted and perpendiculars are drawn from the intersection points to the pressure axis. Zsigmondy explained such a phenomenon by saying that capillary condensation occurred in the *BED* region while water evaporated from capillaries in the *BCD* region. Air adsorbed by dry capillary walls prevents them from being wetted when water is added to silica gel. As a result, contact angles which are formed here by a liquid with capillary walls in silica gel will apparently always be greater than the respective angles in evaporation when the walls are completely wetted with water. Hence, the menisci of a liquid that fills up a capillary will be also less concave in the first case than in the second, and vapour pressure which corresponds to the same amount of liquid adsorbed by silica gel will be greater in hydration than in dehydration.

The curves *BCD* and *BED* have a certain inclination to the pressure axis because silica gel capillaries of different radii are filled up or emptied consecutively. The condensate fills narrow capillaries already at low pressure while considerably higher pressure is required for filling wide capillaries. Of course, an inverse relation is observed when water evaporates from capillaries.

The preliminary thorough removal of air from a porous adsorbent usually greatly reduces hysteresis. This seems to confirm the explanation that hysteresis is caused by the adsorption of air on capillary walls. However, there are also other explanations of this complicated phenomenon. In particular, hysteresis in capillary condensation may be explained by the shape of adsorbent pores. Suppose that an adsorbent has pores which are represented in Fig. 4.10. When a pore is conical (see Fig. 4.10*a*), an adsorption film with a concave surface is formed in it and the spherical surface has the greatest curvature in the narrowest part of the pore. At $p = p_s \exp [-2\sigma V_{mol}/(rRT)]$, vapour is saturated in respect to this surface and begins to condense. The liquid moves to the wider part of the pore, and r increases. For vapour to continue condensing, pressure p must grow (see the isotherm in Fig. 4.10*a*). When p diminishes, the liquid is desorbed from the capillary walls and the isotherm will follow the same way in the opposite direction, i.e., capillary condensation in conical pores is quite reversible.

In cylindrical pores, which are closed at one end, i.e., have the shape of a test tube (see Fig. 4.10*b*), a spherical meniscus is formed at the closed end in adsorption. At $p = p_s \exp [-2\sigma V_{mol}/(rRT)]$, capillary condensation occurs and the pores are filled up with liquid. However, unlike in the preceding case, the meniscus radius here does not change and therefore the pores are filled up at a constant value of p, to which the vertical part of the isotherm for capillary condensation corresponds (see the isotherm in Fig. 4.10*b*). The desorption will occur in the opposite direction in the same way, i.e.,

capillary condensation in cylindrical capillaries having one end closed is also quite reversible.

Lastly, in cylindrical pores which are opened at both ends (see Fig. 4.10*c*), a spherical meniscus cannot be formed in adsorption. Condensation begins on the inner cylindrical meniscus of the film which covers the capillary walls at a pressure of $p_{cyl} = p_s \exp[-\sigma V_{mol}/(rRT)]$. As a result of condensation, the thickness

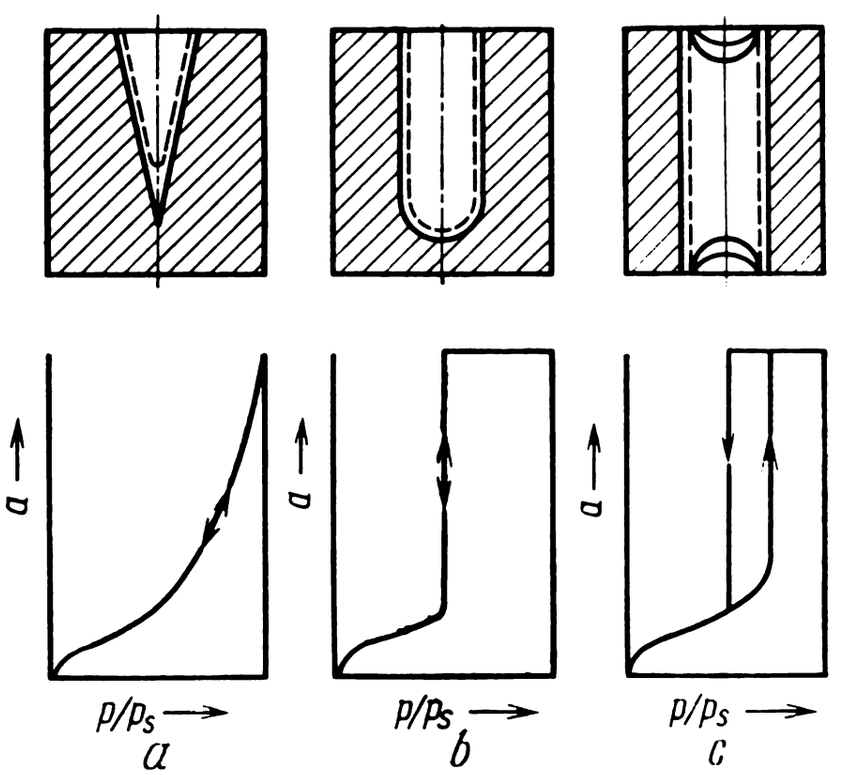


Fig. 4.10. Diagram of capillary condensation in pores having a different shape: *a*—conical; *b*—cylindrical closed at one end; *c*—cylindrical opened at both ends

of the film of a liquid increases while the pore radius decreases, and therefore a pore is filled with liquid at pressure p. The isotherm of capillary condensation, like in the previous case, has a vertical region (see the isotherm in Fig. 4.10*c*). However, owing to the smaller curvature of the cylindrical surface of a meniscus in comparison with that of the spherical surface (when the capillary radius is the same), the vertical region on the isotherm corresponds to higher values of vapour pressure. After a pore is filled up, both of its ends have spherical menisci whose curvature decreases as vapour pressure increases. In desorption, the process occurs reversibly at first, i.e., when small amounts of a liquid evaporate, spherical menisci with a growing curvature are pressed into capillary mouths. However, at $p = p_s \exp[-\sigma V_{mol}/(rRT)]$, these spherical menisci cannot burst open yet and the capillary at this pressure still remains filled up. Only when vapour pressure is reduced to $p = p_s \exp[-2\sigma V_{mol}/(rRT)]$, will the radius of the spherical meniscus be equal to that of the adsorption film in the cylindrical capillary, and will all the liquid

filling up the capillary evaporate. Thus, the desorption curve will diverge from the adsorption one to give a characteristic loop of capillary-condensation hysteresis.

Pores of real adsorbents are not of the same size and shape. They are not filled up or emptied simultaneously. That is why the curves of the hysteresis loop are usually inclined towards the abscissa.

The recuperation (return for use in production) of volatile solvents which are lost in technological processes is based on the phenomena of adsorption and mainly capillary condensation.

For example, let us consider the recuperation of a solvent from glues used in rubber production. In producing rubberized cloths, about 180 kg of rubber glue containing approximately 85 per cent of high-quality benzine are usually spent on a roll of 300 metres. When the cloth is dried after being covered with glue, benzine is volatilized and mixes with air. Hence, an enormous amount of expensive benzine in short supply is lost.

To recuperate the volatile solvent, benzine vapours mixed with air are sucked off from driers when the cloth is being dried, and are fed by means of air pumps to the recuperator which consists of two adsorbers. Benzine vapours enter an adsorber which is filled with activated charcoal. The other adsorber is disconnected during this time. In the first adsorber where the vapour-air mixture has entered, adsorption and then capillary condensation of benzine vapours occur until the adsorbent is completely saturated with the volatile solvent as may be easily established if benzine vapours are no more retained by the charcoal layer. After saturation is attained, the first adsorber is disconnected from the supply tube and the second adsorber is connected to it. Hot steam is fed into the disconnected adsorber in order to evaporate and desorb benzine. Benzine vapour and steam are fed into a cooler and then into a separator where condensed benzine and water are separated as a result of the simple phase separation of these immiscible liquids. During this time, the second adsorber has adsorbed a sufficient amount of benzine and is disconnected from the supply tube in order to carry out the desorption process. The first adsorber is connected now to the tube again. This is how the continuous industrial process of recuperating a volatile solvent is effected.

6. CHEMICAL ADSORPTION

Apart from typical physical adsorption, there is often chemical adsorption, or **chemisorption,** i.e., adsorption which occurs by means of chemical forces. However, there is no pronounced difference between both types of adsorption. Adsorption of the same adsorptive on the same adsorbent may be physical under some conditions, and

chemical, under others. Physical adsorption often precedes chemical adsorption, i.e., the substance is adsorbed by physical forces and is then bound to the adsorbent by chemical forces.

Physical and chemical adsorptions have several distinctions. Physical adsorption is reversible and scarcely specific. The heat of physical adsorption usually constitutes only 2-8 kcal/mol and is commensurable with the heat of condensation. The heat of chemical adsorption may attain 200 kcal/mol, i.e., it is in the range of heats of chemical reactions. Chemical adsorption is usually irreversible

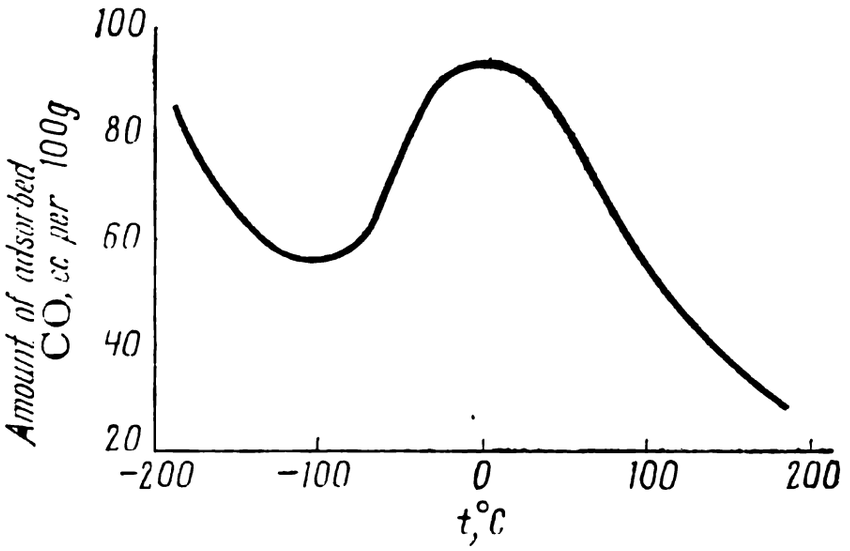


Fig. 4.11. Isobar of adsorption of carbon monoxide by palladium

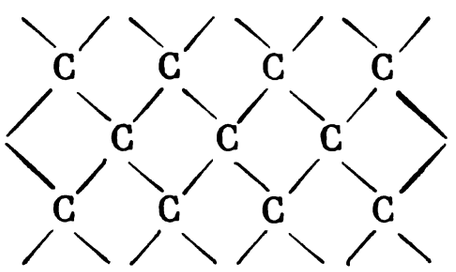
Temperature has a different effect on physical adsorption and on chemical adsorption. Elevated temperature reduces physical adsorption and, conversely, promotes chemisorption because, being a chemical process, chemisorption usually requires considerable activation energy (10-30 kcal/mol). That is precisely why chemisorption is, as a rule, activated adsorption.

Since chemisorption is caused by chemical forces, desorption occurs with great difficulty and, instead of the adsorbed substance another substance is desorbed in most cases. In essence, desorption consists not in the loss of a molecule from the adsorbent surface but in the decomposition of the surface compound that was formed in the course of chemisorption. Chemisorption, like a chemical reaction, is specific, i.e., only definite adsorptives may interact with the adsorbent. An important fact is that activation energy grows with the number of molecules chemisorbed on the surface. This can be explained only by the existence of active centres having different activation energies.

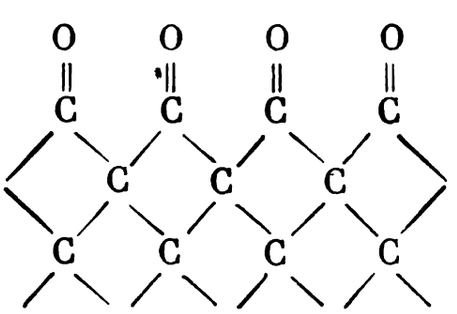
If chemisorption is reversible, the dependence of the amount of the adsorbed substance on temperature may become rather complicated. Figure 4.11 shows the isobar of adsorption of CO by palladium. At low temperatures, there is only physical adsorption which rapidly decreases as temperature rises. However, when a defin

temperature is attained, activated adsorption occurs, and the amount of the adsorbed substance grows with temperature. In this case, for all practical purposes, only chemisorption occurs while physical adsorption becomes very inconsiderable. In the high temperature range, the amount of the adsorbed substance again decreases as a result of its decomposition.

A typical example of chemisorption is adsorption of oxygen on coal. The coal surface apparently has carbon atoms with free valencies, and this may be illustrated schematically in the following way:



Owing to the unsaturation of carbon atoms, oxygen may be adsorbed on the coal surface:



When an effort is made to desorb the adsorptive by heating, molecules of carbon oxides, rather than of oxygen, are driven off from the surface. This indicates that the bond between the atoms of oxygen and carbon is stronger than that between carbon atoms. The monomolecular layers of new compounds which are formed in chemisorption, or *surface compounds*, as N. Shilov called them, cannot be regarded as a new phase, as a new substance. Indeed, a chemical bond is formed between the molecules of an adsorptive and the atoms (molecules) of an adsorbent, but the surface atoms of the adsorbent are still bound to its other atoms. The energy of formation of a chemical bond between the molecules of an adsorptive and those of an adsorbent is apparently insufficient for the surface atoms of the adsorbent to tear away from the crystal lattice. When energy is fed from outside, e.g., when the temperature is raised, it is possible for the atoms to tear away, as a result of which surface reaction becomes ordinary heterogeneous reaction and a new phase is formed.

The heat of surface reactions is usually considerably greater than that of the formation of a chemical compound. For example, the heat of adsorption of oxygen on coal is approximately twice as high as that of the combustion of solid carbon.

Both physical and chemical adsorptions are very important in heterogeneous catalysis because adsorptive molecules react with one another much more rapidly on the catalyst surface. Various scientists have expressed different opinions about the cause of this phenomenon. An adsorbent concentrates and orients on its surface the molecules of components participating in the reaction; it accelerates the reaction but does not participate in it. A reaction may be accelerated on the surface of an adsorbent (catalyst) also because surface forces cause adsorptive molecules to dissociate into more reactive atoms or, at least, weaken the bonds between the atoms of a molecule. The importance of adsorption in heterogeneous catalysis is considered in detail in special textbooks of the physical chemistry of gaseous reactions and catalysis.

7. HEAT OF ADSORPTION

Physical adsorption, as we have already seen, is an exothermal process. The amount of heat liberated in adsorption may be measured by either an isothermal or an adiabatic calorimeter. When the isothermal calorimeter is used, the liberated heat of adsorption is determined, for example, by the amount of ice that has become water. The temperature of the system remains constant in this case, and heat is spent exclusively on phase conversion. When the adiabatic calorimeter is used, the amount of liberated heat is determined by the elevation of temperature in the calorimeter. The values of the heats of adsorption experimentally determined by the calorimeter are often not precise enough because adsorption and, consequently, the liberation of heat take a very long time, which inevitably leads to heat losses.

There are two ways of expressing the heat of adsorption: *integral* and *differential* ways. Let us consider them in somewhat greater detail.

Integral heat of adsorption, q_{int}. This is the total amount of heat dissipated in adsorption per gram of the adsorbent. Apparently,

$$q_{int} = Q/m \tag{4.26}$$

where Q = total amount of dissipated heat, cal;
m = mass of the adsorbent, g.

The unit of measurement of the integral heat of adsorption in conformity with Eq. (4.26) is cal/g (of the adsorbent).

It may seem at first that heat q_{int} should be directly proportional to the amount of the adsorbed substance a. But in fact this is not so

(Fig. 4.12) because, at the beginning of a process, gas is adsorbed on the most active centres with the maximum thermal effect; at the end of the process, adsorption involves less active centres when a comparatively small amount of heat is liberated.

Differential heat of adsorption, q_{dif}. Suppose that at a given moment, n moles of the adsorptive were adsorbed on the adsorbent surface and Q calories of heat were then liberated. Afterwards, dn moles of the adsorptive were additionally adsorbed at the same

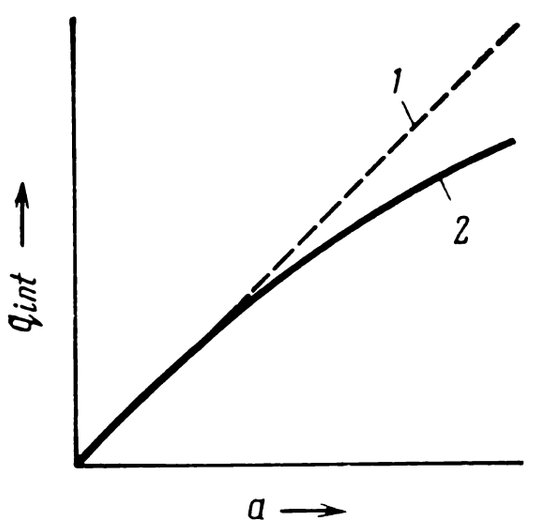


Fig. 4.12. Dependence of the integral heat of adsorption q_{int} on the amount of the adsorbed substance a:
1—when q_{int} is proportional to a; *2*—experimentally obtained dependence

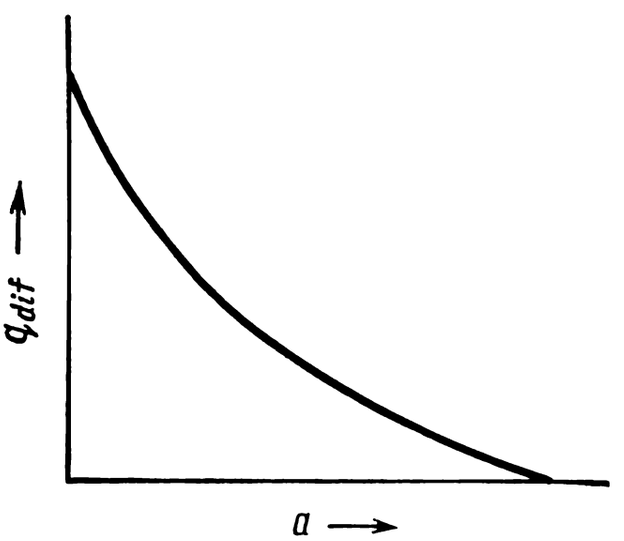


Fig. 4.13. Dependence of the differential heat of adsorption q_{dif} on the amount of the adsorbed substance a

temperature and dQ calories of heat were liberated. The differential heat of adsorption q_{dif} is the ratio of this additionally liberated heat to the additionally adsorbed amount of the adsorptive, i.e.,

$$q_{dif} = dQ/dn \qquad (4.27)$$

In other words, the differential heat of adsorption is the heat liberated per mole of the additionally adsorbed substance. The unit of measurement of the differential heat of adsorption in conformity with Eq. (4.27) is cal/mol (of the adsorptive).

The dependence of the differential heat of adsorption on the amount of the adsorbed substance may be illustrated by a graph, as shown in Fig. 4.13. The differential heat of adsorption decreases in the course of a process because the adsorptive molecules are adsorbed by less and less active centres of the surface as the most active centres become saturated.

The investigation of the heats of adsorption of diverse gases by different surfaces was of great help in understanding the nature of

adsorption processes and phenomena of heterogeneous catalysis, and in solving several practical problems, such as the selection of catalysts.

8. ADSORPTION RATE

The rate of physical adsorption on non-porous adsorbents is usually very high, and therefore its measurement is often very difficult. In many cases, adsorption equilibrium is attained in 10-20 seconds, and 90-95 per cent of the adsorptive is bound with the adsorbent already in 1-2 seconds. For practical purposes it is assumed that the adsorption rate is determined by the rate at which the adsorptive reaches the adsorbent surface, i.e., by the diffusion rate.

Retarded physical adsorption that is sometimes observed may be caused by the adsorbent structure. Adsorbents are often porous,

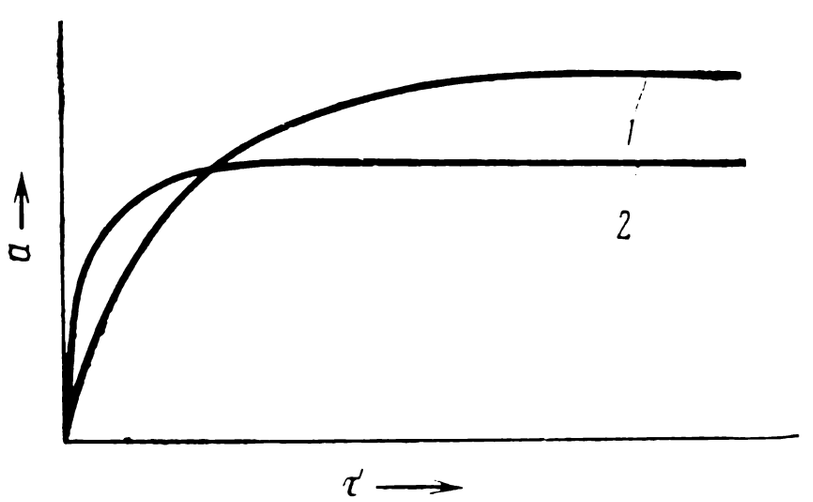


Fig. 4.14. Dependence of the amount of the adsorbed substance on adsorption time τ at different temperatures:
1—curve corresponding to temperature T_1; *2*—curve corresponding to temperature T_2 ($T_1 < T_2$)

and occasionally it takes a long time for adsorptive molecules to penetrate into pores. Physical adsorption may also be retarded if it is accompanied by chemisorption which takes a longer time. Lastly, retarded adsorption may be caused by the presence of adsorbed air or water vapours on the adsorbent surface.

Typical kinetic curves of adsorption are represented in Fig. 4.14. The shape of these curves is explained in the same way as the shape of the adsorption isotherm. At first, adsorption is practically proportional to time because the adsorbent surface is free from the adsorptive. Once adsorption equilibrium has been established, adsorption no longer depends on time and the appropriate segments of curves are almost parallel to the time axis.

The equation for the adsorption rate is usually

$$da/d\tau = k\,(a_{equil} - a_\tau)$$

where a_{equil} = amount of the adsorbed substance that corresponds to adsorption equilibrium under given conditions;
a_τ = amount of a substance adsorbed by time τ;
k = equation constant.

The physical meaning of this equation is quite clear: the closer is a system to equilibrium or the greater is the saturation of a surface, characterized by the factor $(a_{equil} - a_\tau)$, the slower is adsorption. The constant k depends on the area of the adsorbing surface and on the adsorptive diffusion coefficient.

Sometimes, as an equation for the adsorption rate, we use the parabolic equation which is similar to Freundlich's equation

$$a = k\tau^{1/n} \tag{4.28}$$

This equation has the same shortcomings as Freundlich's equation.

Experimentally, the adsorption rate is investigated either by determining, at definite moments, the amount of gas that is still not adsorbed in a system, or by measuring the weight gained by the adsorbent. The McBain balance is widely used for studying the kinetics of adsorption; it consists of a miniature cup which is suspended on a very sensitive spring. A piece of adsorbent is put in the cup, and the spring together with the cup is placed in a vessel containing the adsorptive. As a result of adsorption, the mass of this piece grows and the spring accordingly becomes more stretched. The kinetics of adsorption may be determined by the extent to which the calibrated spring is stretched.

The effect of temperature on the adsorption rate is of certain interest. The adsorption rate increases with temperature because heating always promotes the establishment of equilibrium in a system. On the other hand, as temperature rises, adsorption which conforms to the equilibrium state decreases. Hence, the kinetic curves of adsorption at different temperatures should intersect one another, as is shown in Fig. 4.14.

The temperature coefficient of the physical adsorption rate is not great because the activation energy of physical adsorption approximates zero and the acceleration of adsorption with temperature is mainly caused by increased supply of the adsorptive to the adsorbent surface, i.e., by a higher diffusion rate. In chemisorption, the temperature coefficient of the adsorption rate has the same order as that in chemical processes because the activation energy of chemisorption is high enough and temperature considerably accelerates chemical interaction.

9. EFFECT OF THE PROPERTIES OF THE ADSORBENT AND THE ADSORPTIVE ON ADSORPTION. DYNAMIC ADSORPTION. ADSORPTION FROM MIXTURES OF GASES

Effect of adsorbent properties. As follows from the adsorption theories we have considered, the ability of an adsorbent to adsorb gases is strongly affected by its porosity and also by its physical state. Amorphous adsorbents usually adsorb gas much better than crystalline ones, apparently because the surface of the amorphous adsorbent is rough whereas that of a crystal is smooth except for edges and corners.

Non-porous adsorbents, which are obtained by chemical reactions in a solution and subsequent precipitation (e.g., barium sulphate), and also by grinding solids, usually have a comparatively small surface area (1-10 m^2/g). Therefore, their application is rather limited. Adsorbents of a higher degree of dispersion that have non-porous particles may be obtained upon incomplete combustion of organic compounds (carbon black) or organo-silicon compounds (powdered silica), and also upon hydrolysis of silicon halides ($SiCl_4$, SeF_4) in water vapours (Aerosils). The powders obtained that have a surface area of hundreds of m^2/g are used as fillers of polymers, varnishes, and lubricants.

Highly-dispersed porous adsorbents are usually used as adsorbers, driers, catalysts, or carriers of catalytically active substances. Such adsorbents are used, as a rule, not in the form of powder, but in the form of granules or tablets that are sufficiently strong mechanically. This ensures considerable convenience for their employment (they are not scattered) and reduces their resistance to the flow of a gas or a liquid from which adsorption is effected.

As fine-pored adsorbents, charcoal, animal (bone) charcoal, silica gel, various natural silicates, alumina gel, and aluminosilica gel are most widely used. Charcoal obtained from hard wood is preferable for adsorption because charcoal obtained from soft wood, such as pine wood, is very unstable and readily crumbles. The best grades of carbon for adsorption are obtained from the coconut hull and apricot stones. Moreover, activated charcoal is often used for adsorption.

Ordinary charcoal (raw charcoal) has comparatively small adsorbability because its surface area is rather small and the pores are largely filled with resins and products of incomplete combustion which are formed when charcoal is being obtained. The activation of charcoal consists in thermal treatment, as a result of which its surface area increases whereas products of incomplete combustion partially burn up and partially volatilize. To avoid large losses as

a result of combustion, thermal treatment is effected in an atmosphere of steam or carbon dioxide (at 750-950 °C). Organic substances contained in charcoal, and partially charcoal itself, react with steam and carbon dioxide to form CO and H_2. Since these processes are endothermal, activation in an atmosphere of steam or carbon dioxide can be easily stopped at the moment when unnecessary organic substances burn up and the main part of charcoal is still unaffected.

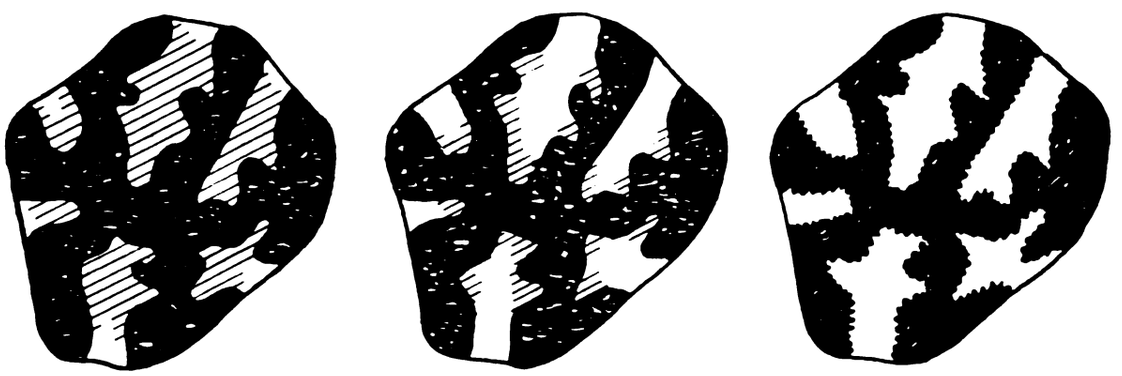


Fig. 4.15. Gradual change in the structure of charcoal as it is activated

The change in charcoal structure during activation is shown in Fig. 4.15 (regions occupied by resins and products of incomplete combustion are crosshatched). The specific surface area of activated charcoal is in the range of 300-1000 m^2/g, and the diameter of micropores is in the range of 30-90 Å.

Charcoal is used as an adsorbent for filling gas masks, recuperating solvents, refining sugar, decolorizing many liquids, and purifying air in industry; it is also used in medicine. Adsorption by activated charcoal should not be confused with activated adsorption.

Another adsorbent often used in practice is silica gel, i.e., hydrated silicon dioxide prepared as a very porous body or a powder. Silica gel is usually obtained by introducing a solution of sodium silicate, with vigorous stirring, into a 5-10 per cent solution of hydrochloric acid. The porous silica gel formed is ground and washed with water. Pieces of it are then dried at about 500 °C, crushed to particles of the required dimensions, and sifted in order to remove dust. The specific surface area of silica gel thus prepared is 400-500 m^2/g. The capillaries of silica gel are somewhat wider than those of activated charcoal, and their dimensions are more homogeneous.

Silica gel differs from charcoal by a smaller adsorbability at very low pressure and also by the ability to selectively adsorb water vapours. Therefore, it is often used for drying gases.

Molecular sieves are now widely used as adsorbents. An example of such sieves is zeolites whose crystals are composed of alternating silicon-oxygen and aluminium-oxygen tetrahedrons and have pores whose diameter ranges from 4 Å to 7.5 Å, depending on the type

of zeolite. Loose three-dimensional lattices of zeolites are capable of adsorbing and retaining rather small molecules whereas large molecules cannot penetrate into these lattices. This is the underlying principle of the molecular-sieve action of zeolites which are used for drying, separating vapour mixtures, and isolating dissolved substances from solutions. In particular, the drying of organic solvents with zeolites is based on the fact that water molecules (whose diameter is 2.75 Å) readily penetrate into the narrow pores of zeolite crystals whereas large molecules of a solvent do not get into such pores.

An important advantage of porous crystals is the high homogeneity of their pore dimensions.

Effect of adsorptive properties. As we have already seen, N. Saussure established that gas is adsorbed the better, the more readily it is liquefied, i.e., the higher is its critical temperature. Later, it was established that gas adsorption is the greater, the higher is the boiling point of a substance. It was also ascertained that adsorption and the heat of gas evaporation were connected. Lastly, S. Arrhenius discovered that the amount of adsorbed gas increases with a growth in the constant a in the well-known van der Waals equation.

Table 4.1 gives data which characterize the connection between adsorption and the physical properties of some gases.

Table 4.1. **Dependence of the Adsorption of Gases by Charcoal on Their Physical Properties**

Gas	Molecular weight	Boiling, point, K	Critical temperature, K	Volume of gas (in cc) adsorbed by a gram of charcoal at 15 °C
SO_2	64	263	430	379.7
NH_3	17	240	405	180.9
N_2O	44	183	309	54.2
C_2H_2	26	189	308	48.9
CO_2	44	195	242	47.6
CO	28	81	134	9.3
N_2	28	77	126	8.0
H_2	2	20	33	4.7

It follows from Table 4.1 that the boiling point, the critical temperature of a substance, and adsorption are interconnected. Since the boiling point is usually two-thirds of the critical temperature,

adsorption which increases with the critical temperature should increase also with the boiling point. The connection between the physical properties of gases and adsorption is obvious because the forces which are involved in liquefaction of gases and their adsorption are similar in nature.

The connection between adsorption and the given physical parameters of gases is exhibited only in physical adsorption. In chemisorption, owing to its specific nature, such a connection is usually absent.

Dynamic adsorption. Everything that was said earlier about adsorption relates to the case when it occurs under *static* conditions, i.e., when an adsorbent adsorbs molecules from the same gas volume until adsorption equilibrium is established. However, in practice, of great importance is *dynamic* adsorption when the gas to be adsorbed, or its mixture with air, is passed through an adsorbent layer. Such conditions exist during the operation of units in which solvent vapours are recuperated from a mixture with air, during the operation of the gas mask, and so forth.

The dynamic activity of an adsorbent differs considerably from its static activity. Static adsorption activity at a given temperature and concentration of a gas is determined by the amount of the substance absorbed per unit mass of an adsorbent when equilibrium is being established. The dynamic activity of the adsorbent is characterized by the time it takes for a gas or its mixture with air to pass through the adsorbent layer until the first traces of gas are detected behind the adsorbent layer. This quantity depends on the static activity of the adsorbent and also on other factors, i.e., on the ratio between the thickness and the area of the adsorbent layer, the diameter of adsorbent grains, the concentration of gas, and the rate of its flow. Therefore, dynamic adsorption may be characterized only by the time taken for the first traces of a gas to be detected behind the adsorbent layer under given conditions of a process, and it cannot be described by the amount of gas adsorbed per unit mass or unit volume of the adsorbent. The dynamic activity of the adsorbent has been thoroughly studied in the Soviet Union by N. Shilov, and later by M. Dubinin and other scientists.

Adsorption of gases from their mixtures. The adsorption of gases from their mixtures is of great practical importance because the conditions under which the adsorbent is surrounded by the atmosphere of a single gas are found very rarely in practice. The adsorption of gases from their mixtures with air is involved in the recuperation of solvents, in air conditioning, and in the purification of carbon dioxide, molecular hydrogen, and ammonia.

Each gas is adsorbed always less from a gaseous mixture than when it is adsorbed alone. The better the adsorption of a gas, the greater is it adsorbed from the mixture. One gas may be adsorbed from the mixture to such an extent that another gas is practically not adsorbed. In particular, when vapours of organic solvents are adsorbed from the air by activated charcoal, the effect of air on their adsorption is negligible.

One should never forget that an adsorbent to be used could have adsorbed a gas earlier. Then, adsorption will be only the displacement of one gas by another from the adsorbent surface.

5

ADSORPTION AT THE SOLUTION—GAS INTERFACE

The molecular-kinetic concepts which we widely used in the preceding chapter are hardly suitable for considering the phenomena of adsorption of a dissolved substance at the solution—gas interface. In this case, it is far more expedient to consider the phenomena from the thermodynamic standpoint and connect the adsorption of a dissolved substance with a change in free energy of the surface or surface tension.

Owing to the homogeneity and smoothness of the surface of any liquid, the ordinary concepts of active centres are quite inapplicable when adsorption on the liquid surface is being studied. Apparently, we cannot also speak of the attachment of adsorptive molecules in definite places either, due to the equivalence of all the regions of the surface of a liquid and to the thermal motion of its molecules. Molecules of the adsorptive are capable of freely moving on the surface and, as a rule, they are in thermal motion, provided they are not bound to one another by molecular forces.

1. SURFACE TENSION

The science of surface tension and the methods of determining it are considered in detail in physics textbooks. Here, only some information on the surface tension of liquids and solids will be given.

Surface tension is the result of the existence of internal pressure, i.e., a force which draws molecules into a liquid and which is perpendicular to the surface. The greater the polarity of a substance, the higher is internal pressure because this pressure is caused by the action of molecular forces. For example, the internal pressure of water is 14,800 atm whereas that of benzene is only 3800 atm. The great values of internal pressure explain why liquids are poorly compressible under the action of external pressures which are usually used in practice.

Internal pressure draws in molecules that are located on a liquid surface and thus tends to bring the surface to a minimum under given conditions. The force which acts per unit length of an interface and causes a diminution of the liquid surface is known as the *force of surface tension* or simply *surface tension*. The unit of measurement of this quantity is dyn/cm. This force is always tangential to the liquid surface.

In order to increase the liquid surface, work must be done to overcome forces which cause internal pressure. Work which is necessary for creating unit surface in a reversible and isothermal process is equal to the specific free energy of a surface. Obviously, the unit of measurement of this quantity is erg/cm^2. Since erg = dyn·cm, units of measurement which are the same for surface tension can be obtained for the specific free surface energy, or work in creating one square centimetre of surface, i.e., dyn/cm. The specific free surface energy is numerically equal to surface tension; both of these quantities are denoted by the symbol σ. Free surface energy is equal to surface tension only for a single-component liquid.

Under the action of surface tension, when external forces are absent, a liquid always tends to assume a spherical shape because the surface of a sphere is the smallest surface that limits the volume, and therefore the surface energy of a system will be then at a minimum.

Table 5.1 gives the values of σ of some substances in the liquid state at the interface with air or with vapour of the same liquid.

Table 5.1. **Surface Tension of Some Substances in the Liquid State at the Interface with Their Vapours or Air**
(according to I. Zhukov)

Liquid	Temperature, °C	σ, erg/cm^2	Liquid	Temperature, °C	σ, erg/cm^2
Mercury	20	485	Hexane	20	18.5
Water	20	72.75	Gold	1200	1120
Glycerol	20	66.0	Tin	900	510
Ethylene glycol	20	46.7	Sodium chloride	811	113
Aniline	20	42.9	Oxygen	—198	17
Benzene	20	28.9	Hydrogen	—252	2
Chloroform	20	27.1	Helium	—270	0.24
Ethanol	20	21.6			

Surface tension is proportional to internal pressure. Therefore the greater the intermolecular interaction, the higher the surface tension.

The value of surface tension in the formation of a surface for an individual liquid is established practically instantaneously, approximately in the course of 0.001 sec.

As temperature rises, the surface tension of liquids diminishes almost according to the linear law. This means that the temperature coefficient $d\sigma/dT$ has an almost constant negative value up to temperatures which are close to the critical temperature. At the critical temperature, the difference between boundary phases disappears and surface tension becomes zero. This applies not only to the liquid—vapour system, but also to the liquid—liquid system when surface tension disappears at the critical temperature of solubility.

The surface tension at the liquid—gas or the liquid—vapour interface is determined by the methods of the capillary rise, the weighing or counting of drops, the maximum bubble pressure, the break-off of the ring, and several other methods described in physics textbooks and courses in practical colloid chemistry.

We have considered above the surface tension at the liquid—gas or the liquid—vapour interface. For these systems, the interaction between molecules of a liquid and a gas or vapour can be neglected owing to the great rarefaction of a gas or vapour. Of course, this cannot be done in the case of surface tension at the liquid—liquid interface. When a layer of a liquid is overlaid by a layer of another liquid that is immiscible with it, interfacial surface tension decreases since the molecules of the latter liquid attract the molecules of the former and thus reduce the action of uncompensated forces on the surface of the former liquid. A decrease in interfacial surface tension is apparently more considerable, the smaller is the difference in the polarities of both liquids. Liquids which are similar by their polarity

Table 5.2. **Surface Tension at the Interface of Mutually Saturated Liquids (Liquid — Water) and at the Interface of These Liquids and Air**
(according to I. Zhukov)

Liquid	Temperature, °C	σ at the interface with air, erg/cm²		σ at the liquid — water interface, erg/cm²	
		water layer	organic layer	estimated value	experimental value
Benzene	19	63.2	28.8	34.4	34.4
Aniline	26	46.4	42.2	4.2	4.8
Chloroform	18	59.8	26.4	33.4	33.8
Carbon tetrachloride	17	70.2	26.7	43.5	43.8
Amyl alcohol	18	26.3	21.5	4.8	4.8
Cresol	18	37.8	34.3	3.5	3.9

mix with one another in all ratios, and therefore surface tension between them should be zero. If liquids are finitely soluble in one another, then as G. Antonov showed as early as 1907, surface tension at the liquid—liquid interface is close to the difference between surface tensions of mutually saturated liquids at their interface with air (Antonov's rule). Table 5.2 gives data which show the extent to which Antonov's rule conforms to reality if one of the liquids is water.

Surface tension at the liquid—liquid interface can be determined by methods which are in many respects similar to those used for finding surface tension at the liquid—gas interface.

The surface tension of solids can be determined only by indirect methods. Table 5.3 gives the values of surface tension of some crystals found by the solubility method. This method is based on W. Thomson's (Kelvin's) law which connects the solubility of a substance with the dimensions of its small particles and surface tension.

Table 5.3. **Surface Tension of Some Crystals** (according to I. Zhukov)

Crystals	Temperature, °C	σ, erg/cm²
CaF_2	30	2500
$SrSO_4$	30	1400
$BaSO_4$	25	1250
PbF_2	25	900
$AgCrO_4$	26	575
$CaSO_4 \cdot 2H_2O$	30	270
PbI_2	30	130

It should be noted that when surface tension of crystals in general is concerned, certain averaging is allowed because diverse crystal faces have different surface tension, depending on how densely atoms or ions fill these faces and, consequently, on how intensely molecular forces act.

2. CONCEPT OF SURFACTANTS

We have considered above the concepts of surface tension of individual liquids. Adsorption strongly affects the surface tension of solutions.

All soluble substances can be divided into two groups according to their ability to be adsorbed at the liquid—air interface: surface-active substances and surface-inactive substances.

Surface-active substances. These substances which are also called *surfactants* are capable of accumulating in the surface layer. Consequently, *positive adsorption* would occur in this case, i.e., $\Gamma > 0$. Surfactants must possess surface tension which is less than that of a solvent: otherwise, the accumulation of a substance in the surface layer is thermodynamically disadvantageous. Their solubility must be comparatively small or they would tend to sink from the surface into the depth of a liquid. In other words, the interaction between the molecules of a surfactant (taken as a whole) and of a solvent is always less than that between the molecules of the solvent. Therefore, surfactants will be pushed out from the solution volume to the surface, i.e., $\Gamma > 0$. As a result of the accumulation on the solution surface of surfactant molecules which poorly interact with one another, intermolecular interaction in the surface layer and surface tension decrease.

Surfactants for water include many organic compounds: fatty acids having a rather large hydrocarbon radical, salts of these acids (soaps), sulphonic acids and their salts, alcohols, and amines. A characteristic of the molecular structure of most surfactants is their diphilic nature, i.e., a molecule consists of two parts: a polar group and a non-polar hydrocarbon radical. A polar group has a considerable dipole moment, is well hydrated, and engenders the affinity of a surfactant for water. A hydrophobic hydrocarbon radical is the cause of low solubility of these compounds in water. The smallest value of surface tension of an aqueous solution of surfactants may be 25 erg/cm^2, i.e., it is almost equal to the value of surface tension of hydrocarbons.

Hereafter, we will represent diphilic molecules of a surfactant by the generally accepted symbol

where the circle denotes the polar group, and the line, or the tail, the non-polar radical.

Surface-inactive substances. These substances tend to go away from the liquid surface into the volume, as a result of which *negative adsorption* occurs, i.e., $\Gamma < 0$. Surface-inactive substances have surface tension which is greater than that of a solvent: otherwise, they would spontaneously accumulate in the surface layer. They usually possess high solubility which favours their tendency to submerge into the volume of a liquid. In other words, the interaction between the molecules of a surface-inactive substance and of a solvent is always greater than that between the molecules of the solvent. Therefore, surface-inactive substances tend to pass over into the solution volume.

Surface-inactive substances include all the inorganic electrolytes: acids, alkalis, and salts. The molecules of these substances do not have a hydrophobic moiety and disintegrate in water into well-hydrating ions. Monovalent ions cause a comparatively small increase in surface tension. Bivalent ions are more effective than monovalent ones in equimolecular solutions.

Organic surface-inactive substances in respect to water include only ionizing substances whose non-polar moiety is either absent or very small, for example, formic and aminoacetic acids.

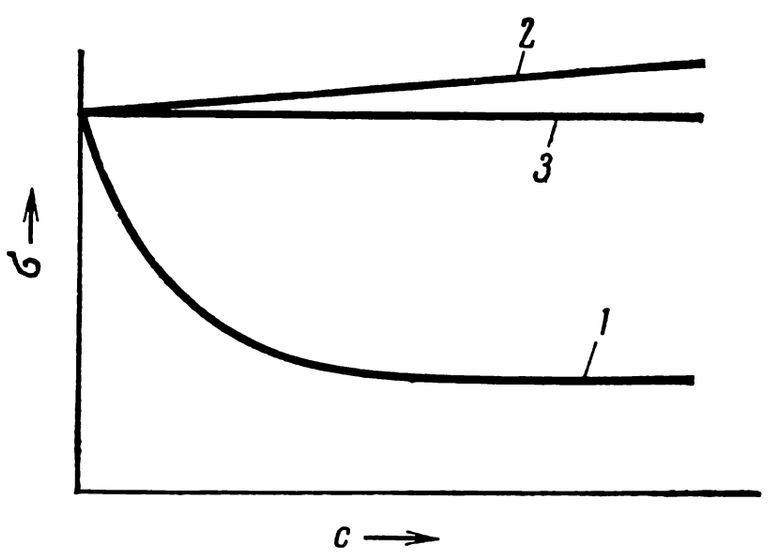


Fig. 5.1. Dependence of surface tension σ on the concentration of a solution *c*: *1*—isotherm for a surfactant; *2*—the same for a surface-inactive substance; *3*—the same for a substance which does not affect the surface tension of a solvent

In non-aqueous solvents, inorganic electrolytes also increase surface tension, the effect depending on the nature of a solvent. For example, surface tension greatly increases when sodium iodide is introduced into methanol, and about half as much in the case of ethanol. The effect is even smaller in alcohols of higher molecular weight.

Substances which do not affect the surface tension of a solvent are distributed uniformly between the surface layer and the volume of a solution, and for them $\Gamma = 0$. Such substances have surface tension which is similar to that of a solvent. An example of substances which are poorly active towards water are sugars: the surface tension of water remains almost unchanged when sugars are dissolved in it. However, though sugars do not noticeably change surface tension at the interface of an aqueous solution and air, they often turn out to be surface-active at the interface of an aqueous solution and another liquid or a solid phase.

Figure 5.1 gives the isotherms of surface tension, i.e., curves which characterize a change in surface tension as the concentration of a substance increases. The isotherm at first sharply drops almost in a straight line as the concentration of a surfactant increases (curve *1*)

because at first the liquid—air interface is free of a surfactant, and almost all small quantities of it present in a solution go to the surface. Then comes a curvilinear segment of the isotherm which corresponds to the average concentrations of a surfactant. Under these conditions, a considerable part of the surface is occupied by the molecules of a surfactant, and this reduces its further adsorption at the interface. Lastly, large concentrations of a surfactant are represented by an almost horizontal segment of the isotherm which shows that surface tension depends little on concentration. Under these conditions, a continuous monomolecular layer of a surfactant is formed on the liquid surface and further adsorption is impossible.

The isotherm rises slantwise as the concentration of a surface-inactive substance increases in a solution (curve *2*) because surface-inactive substances go into the volume owing to great surface tension and good solubility, whereas the liquid—air interface has only a small portion of this substance which gets there by diffusion from the solution volume.

Lastly, when the concentration of substances which do not affect surface tension increases (curve *3*), the isotherm is a straight line parallel to the concentration axis.

The surface activity of a substance depends not only on its nature, but also on the properties of a solvent (medium). If the solvent has high surface tension, the substance may exhibit considerable surface activity; if the solvent has low surface tension, the same substance may become surface-inactive. Water, which is the most commonly used solvent, has high surface tension, and therefore many substances exhibit surface activity to it. Alcohols have considerably less surface tension than water. Therefore, some substances are surface-active to water, and inactive, to alcohols.

Establishment of the equilibrium value of surface tension. The balance of molecular forces on the newly formed surface of individual liquids and, consequently, the equilibrium value of surface tension are established practically instantaneously. Equilibrium concentration of a surfactant should be established on the surface of surfactant solutions, and this is effected by diffusion. Therefore, it may take a long time to establish the equilibrium value of surface tension at the solution—air interface if the molecules of a surfactant are large and diffuse slowly, such as the molecules of higher fatty acids and their salts.

Dependence of surface tension on temperature. The dependence of surface tension of surfactant solutions on temperature, studied by P. Rehbinder, is unique. The surface tension of individual liquids steadily decreases with temperature. The surface tension of solutions of some surfactants may change, with an elevation of temperature,

according to the curve which has a maximum. Figure 5.2 schematically illustrates the temperature dependence of surface tension for individual liquids (*1*) and solutions of such surfactants (*2*). The

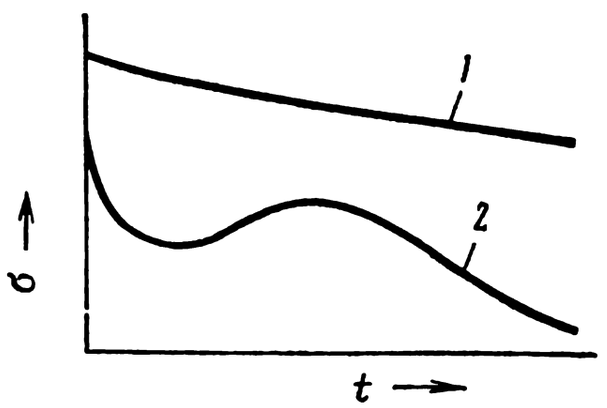


Fig. 5.2. Dependence of surface tension σ on temperature *t*:
1—individual liquid; *2*—solution of a surfactant

maximum on curve *2* is caused by the desorption of a surfactant at a certain temperature range, and this increases surface tension. At higher temperatures, surface tension begins to decrease again after desorption ends.

3. GIBBS' EQUATION

To interpret adsorption phenomena at the solution—gas interface, it is important to establish the connection between Γ, the excess of an adsorbed substance in the surface layer, *c*, the concentration of a surfactant in a solution, and σ, surface tension at the solution—gas interface. This connection for dilute solutions is given by Gibbs' equation of adsorption derived in 1876

$$\Gamma = -\frac{c}{RT} \cdot \frac{d\sigma}{dc} \tag{5.1}$$

Let us present a simplified derivation of Gibbs' equation that was given by W. Ostwald.

Suppose that a surfactant solution has surface ω and surface tension σ, and that the surface layer of this solution has an excess of one mole of the surfactant substance. Apparently, in this case

$$\Gamma = 1/\omega \tag{5.2}$$

Suppose that the volume of the solution contains also one mole of the surfactant. Let us imagine that a very small amount of the surfactant was transferred from the volume to the surface layer. In this case, surface tension will change by the quantity $d\sigma$.

Since the system was in equilibrium at first, the transfer of the substance from the volume to the surface layer will require a certain

amount of work $V\,d\pi$ to overcome osmotic pressure (where V is the solution volume, and $d\pi$, a difference in osmotic pressures before and after the transfer).

Since the change in surface energy should be equal to the value of osmotic work done with an opposite sign, we may write

$$\omega\,d\sigma = -V\,d\pi$$

But since $V = RT/\pi$, and because π for sufficiently diluted solutions is proportional to concentration c, the last equation may be represented as

$$\omega\,d\sigma = -\frac{RT\,d\pi}{\pi} = -\frac{RT\,dc}{c} \tag{5.3}$$

Substituting the value of ω found from Eq. (5.2) in this equation and solving it in respect to Γ, we obtain Gibbs' equation

$$\Gamma = -\frac{c}{RT}\cdot\frac{d\sigma}{dc}$$

When sufficiently concentrated solutions are involved, concentration c in Gibbs' equation should be replaced by a, the activity of a substance.

Let us give an additional, stricter derivation of Gibbs' equation which is based on the chemical potential.

As we know from thermodynamics, for a system which consists of two components, the connection between the isobar-isothermal potential G and the chemical potentials μ_1 and μ_2 of both components is expressed by the equation

$$G = \mu_1 n_1 + \mu_2 n_2$$

where n_1 and n_2 are the number of moles of the first and second components, such as a solvent and a dissolved substance.

This equation takes no account of the possibility of a change in the surface of a system. For a real solution having a surface, the term σs (where σ is the surface tension, and s is the surface area) should be introduced into the equation. The foregoing equation can then be written as

$$G = \sigma s + \mu_1 n_1 + \mu_2 n_2$$

After differentiation, we have

$$dG = \sigma\,ds + s\,d\sigma + \mu_1\,dn_1 + n_1\,d\mu_1 + \mu_2\,dn_2 + n_2\,d\mu_2 \tag{5.4}$$

We know from thermodynamics that

$$dG = -S\,dT + V\,dp + \mu_1\,dn_1 + \mu_2\,dn_2$$

where S = entropy;
V = volume;
p = pressure.

This equation also takes no account of the possibility of a change in the surface. When the appropriate correction is made, we get

$$dG = -S\,dT + V\,dp + \sigma\,ds + \mu_1\,dn_1 + \mu_2\,dn_2 \qquad (5.5)$$

Equating the right-hand members of Eqs. (5.4) and (5.5), we obtain

$$S\,dT - V\,dp + s\,d\sigma + n_1\,d\mu_1 + n_2\,d\mu_2 = 0$$

At constant temperature and pressure, this equation is simplified to

$$s\,d\sigma + n_1\,d\mu_1 + n_2\,d\mu_2 = 0 \qquad (5.6)$$

The solution under consideration may be represented as being formed out of two parts: a part under the action of surface forces (the surface phase) and a part which is not under the action of these forces (the volume). Let us denote the number of moles of the first and second components in the volume by n_1^0 and n_2^0, and the number of moles of the same components in the surface phase, by n_1 and n_2.

Apparently, Eq. (5.6) is suitable for the surface phase, and the following equation for the volume:

$$n_1^0\,d\mu_1 + n_2^0\,d\mu_2 = 0 \qquad (5.7)$$

Let us solve Eq. (5.7) in respect to $d\mu_1$:

$$d\mu_1 = -\frac{n_2^0}{n_1^0}\,d\mu_2$$

Substituting the value of $d\mu_1$ in Eq. (5.6), we obtain

$$s\,d\sigma + \left(n_2 - \frac{n_1 n_2^0}{n_1^0}\right) d\mu_2 = 0$$

or

$$-\frac{d\sigma}{d\mu_2} = \frac{n_2 - n_1 n_2^0/n_1^0}{s} \qquad (5.8)$$

where n_2 is the number of moles of a solute that is bound with n_1 moles of a solvent in the surface phase, and $n_1 n_2^0/n_1^0$ is the number of moles of a solute that is bound with n_1 moles of a solvent in the volume.

The right-hand member of Eq. (5.8) represents an excess of a solute per unit surface, i.e., the adsorption quantity Γ. Then, Eq. (5.8) will be

$$\Gamma = -d\sigma/d\mu_2 \qquad (5.9)$$

Since for dilute solutions, $\mu_2 = \mu_2^0 + RT \ln c$, then, at constant temperature, $d\mu_2 = RT\,d \ln c$. Substituting this value of $d\mu_2$ in Eq. (5.9), we obtain Gibbs' equation

$$\Gamma = -\frac{c}{RT}\,\frac{d\sigma}{dc}$$

It follows from Gibbs' equation that if surface tension increases with concentration c, i.e., if $d\sigma/dc > 0$, then $\Gamma < 0$. In other words, the concentration of a solute in the surface layer is less than in the volume (negative adsorption). Conversely, if σ decreases as c increases, i.e., if $d\sigma/dc < 0$, then $\Gamma > 0$, and the concentration of a solute is greater in the surface layer than in the volume (positive adsorption). Lastly, if σ does not depend on c, the concentration of a solute in the surface layer is the same as that in the volume (adsorption is not observed).

The quantity $-d\sigma/dc$ is known as *surface activity*. The quantity, taken on the almost rectilinear region of the isotherm for surface tension when the concentration of a solute is not great and its value is constant, may be a measure of surface activity of a given substance.

In Gibbs' honour, the quantity $-d\sigma/dc$ is denoted by G and is called *gibbs*. Gibbs' equation in this case assumes a very simple form

$$\Gamma = \frac{c}{RT} G \qquad (5.10)$$

whence

$$G = -\frac{d\sigma}{dc} = RT\frac{\Gamma}{c} \qquad (5.11)$$

As follows from Eq. (5.11), the unit of measurement of G is erg·cm/mol.

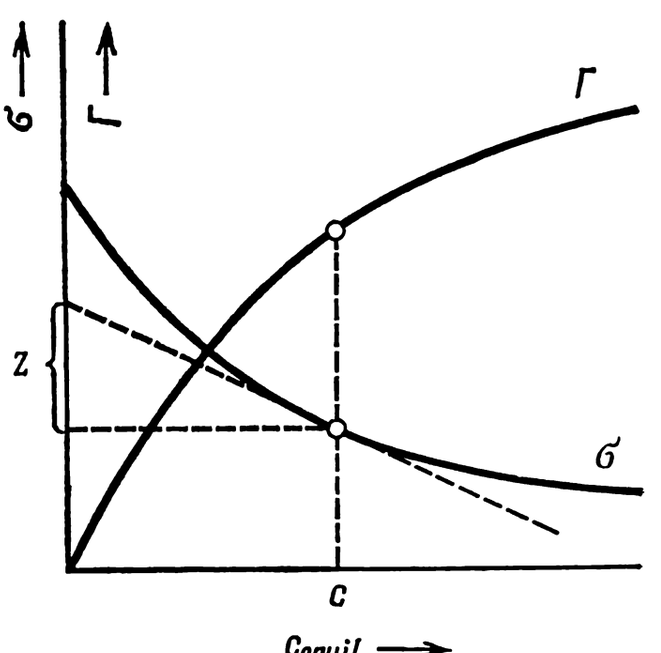


Fig. 5.3. Plotting the adsorption isotherm according to the surface tension isotherm

Gibbs' equation was introduced on the basis of thermodynamic concepts. It is very difficult to experimentally verify the equation owing to the complexity of determining the concentration of a solute in the surface layer. Nevertheless, J. McBain's experiments, in which a very thin liquid layer was cut off from the surface of a solution by means of a device similar to a microtome, have shown that, in all cases studied, the empirical values of adsorption within the limits of experimental error were the same as the values calculated by Gibbs' equation. The correctness of Gibbs' equation was also confirmed by A. Frumkin's experiments.

It is easy to plot the relevant adsorption isotherm, using Gibbs' equation and the isotherm of surface tension for a surfactant. To this end, let us take a point on the isotherm of surface tension and draw through it a tangent and straight lines parallel to the coordinate axes, as shown in Fig. 5.3. The ratio between the segment, which is cut off

on the ordinate by the tangent and the straight line parallel to the concentration axis, and the segment cut off on the abscissa by a straight line drawn through a point parallel to the ordinate, is

$$\frac{z}{c} = -\frac{d\sigma}{dc}$$

Substituting the value found for $-d\sigma/dc$ in Gibbs' equation, we obtain

$$\Gamma = -\frac{c}{RT} \cdot \frac{d\sigma}{dc} = \frac{z}{RT}$$

After determining the respective values of the quantity Γ for several points of the isotherm of surface tension, it is easy to plot the adsorption isotherm.

4. SHISHKOVSKY'S EQUATION. TRANSITION FROM GIBBS' EQUATION TO LANGMUIR'S EQUATION

At low concentrations of a surfactant, the surface tension of a solution σ decreases in direct proportion to concentration c, i.e.,

$$\Delta = \sigma_0 - \sigma = kc \qquad (5.12)$$

where Δ = decrease in surface tension;
σ_0 = surface tension of a pure solvent;
k = constant.

At comparatively high concentrations, a decrease of σ in time with an increase of c is described by the empirical equation proposed by B. Shishkovsky in 1908:

$$\Delta = \sigma_0 - \sigma = \sigma_0 B \ln\left(\frac{c}{A} + 1\right) \qquad (5.13)$$

where B = constant which depends little on the nature of a surfactant and is equal to 0.2 at a temperature of ca. 20 °C;
$1/A$ = *specific capillary constant* which is characteristic of every surfactant.

Shishkovsky's equation is suitable for calculating the surface tension of fatty acids with the number of carbon atoms in a molecule less than eight.

As Langmuir showed in 1917, when Shishkovsky's equation is used differentially, a transition can be made from Gibbs' equation to Langmuir's equation. Indeed, Shishkovsky's equation can be

written as

$$\sigma_0 - \sigma = \sigma_0 B \ln\left(\frac{c}{A} + 1\right) = \sigma_0 B \ln\frac{c+A}{A} = \sigma_0 B \ln(c+A) - \sigma_0 B \ln A$$

Differentiating this equation, we obtain

$$-d\sigma = \sigma_0 B d \ln(c+A) = \frac{\sigma_0 B\, dc}{c+A} \tag{5.14}$$

or

$$-\frac{d\sigma}{dc} = \frac{B\sigma_0}{A+c} \tag{5.15}$$

Substituting Shishkovsky's equation in a differentiated form in Gibbs' equation, we obtain

$$\Gamma = -\frac{c}{RT}\cdot\frac{d\sigma}{dc} = \frac{c}{RT}\cdot\frac{B\sigma_0}{A+c} = \frac{B\sigma_0}{RT}\cdot\frac{c/A}{1+c/A}$$

Denoting $B\sigma_0/RT$ by α_{max}, and $1/A$ by k, and taking into account that at low concentrations, Γ is practically equal to α, we have

$$\alpha = \alpha_{max} kc/(1+kc) \tag{5.16}$$

Since the quantity of adsorption a is proportional to α, we may write

$$a = a_{max} kc/(1+kc)$$

Hence, we have arrived at Langmuir's equation. In this case, the constant $1/A$ in Shishkovsky's equation which is a measure of capillary activity of a substance is equal to the constant k in Langmuir's equation. Hence, Shishkovsky's equation is the bridge between Gibbs' equation, derived on the basis of thermodynamic concepts, and Langmuir's equation, derived on the basis of molecular-kinetic principles.

Using Shishkovsky's equation differentially, we may also find the connection between surface activity $-d\sigma/dc$ and the specific capillary constant $1/A$. Indeed, when concentrations of a surfactant are $c \ll A$, Eq. (5.15) becomes

$$-\frac{d\sigma}{dc} = B\frac{\sigma_0}{A} = \frac{1}{A} B\sigma_0 \tag{5.17}$$

Using Eq. (5.15), we may establish the meaning of the empirical constant B in Shishkovsky's equation. When the concentration is high enough, i.e., when $A \ll c$, the quantity A can be neglected and Eq. (5.15) will be

$$-\frac{d\sigma}{dc} = \frac{B\sigma_0}{c}$$

Substituting this equality in Gibbs' equation, where the quantity $\Gamma = \Gamma_{max} = \text{const}$ at high values of c, we obtain

$$\Gamma_{max} = B\sigma_0/RT$$

whence

$$B = \Gamma_{max} RT/\sigma_0 \qquad (5.18)$$

Since the values of Γ_{max} are the same for all the substances of any homologous series and scarcely differ for ordinary surfactants (fatty acids, alcohols, etc.), it is clear why B is a constant.

5. EFFECT OF THE STRUCTURE AND DIMENSIONS OF A SURFACTANT MOLECULE ON ADSORPTION AT THE SOLUTION—GAS INTERFACE. TRAUBE'S RULE

As we have already seen, surfactant molecules are usually diphilic, i.e., they have a polar and a non-polar part. The polar part of surfactant molecules may be groups which have a sufficiently large dipole moment: —COOH; —OH; —NH_2; —SH; —CN; —NO_2; —NCS; —CHO; —SO_3H. The non-polar part of a surfactant molecule is usually an aliphatic or aromatic radical. The length of a hydrocarbon radical strongly affects the surface activity of a molecule. P. Duclaux and then I. Traube investigated the surface tension of aqueous solutions of a homologous series of saturated fatty acids. They found that the surface activity of these substances at the solution—air interface increases with the length of the hydrocarbon radical, on the average by 3.2 times per CH_2 group. This is easily proven by the fact that the isotherms of surface tension for a homologous series of fatty acids are almost completely superposed if the scale of values on the concentration axis is changed by 3.2 times when a transition is being made from one member of a series to the next.

Another formulation of the Duclaux-Traube rule is: when the length of a fatty acid chain grows arithmetically, surface activity increases geometrically. There should be such a relation also for the quantity $1/A$ in the elongation of a molecule since the surface activity of substances at sufficiently low concentrations is proportional to the specific capillary constant.

The cause of dependence established first by Duclaux and then, in a more general form, by Traube is that the solubility of a fatty acid decreases as the length of its hydrocarbon chain increases, and thus its molecules have a stronger tendency to pass from the volume to the surface layer. For example, butyric acid mixes with water at all ratios; valeric acid forms only a 4 per cent solution; all the other

fatty acids having a higher molecular weight are even less water-soluble.

According to Langmuir, the Duclaux-Traube rule can be substantiated as follows. Suppose that the thickness of the surface layer is equal to δ. The average concentration in this layer will then be Γ/δ. We know from thermodynamics that the maximum amount of work A required for compressing a gas from volume V_1 to volume V_2 can be represented as

$$A = RT \ln (V_1/V_2) \tag{5.19}$$

For two ideal solutions having concentrations of c_1 and c_2 respectively, when $\pi_1 V_1 = \pi_2 V_2$ or $(V_1/V_2) = (\pi_2/\pi_1)$, we may write

$$A = RT \ln (\pi_2/\pi_1) = RT \ln (c_2/c_1) \tag{5.20}$$

where π is osmotic pressure.

The work of adsorption, i.e., the work of a reversible transfer of one mole of a dissolved substance from the volume to the surface layer, will then be

$$A = RT \ln \frac{\Gamma/\delta}{c} = RT \ln \frac{\Gamma}{\delta c} \tag{5.21}$$

Denoting the maximum work of adsorption for two adjacent homologues by A_n and A_{n-1}, we obtain

$$A_n - A_{n-1} = RT \ln \frac{(\Gamma/\delta c)_n}{(\Gamma/\delta c)_{n-1}} = RT \ln 3 = 640 \text{ cal/mol} \tag{5.22}$$

It follows from this equation that the work of adsorption should increase by a constant value when the hydrocarbon chain is elongated by a CH_2 group. This means that at small concentrations—the only ones at which the Duclaux-Traube rule is observed—all the CH_2 groups in the chain occupy the same position in respect to the surface;

Table 5.4. **Dependence of G and $1/A$ on the Length of Fatty Acid Molecules (according to I. Zhukov)**

Acid	G, erg·cm/mol	$\frac{G_{n+1}}{G_n}$	$1/A$	$\frac{(1/A)_{n+1}}{(1/A)_n}$
Acetic, CH_3COOH	—	—	2.84	3.1
Propionic, C_2H_5COOH	8.5×10^4	3.4	8.93	2.2
n-Butyric, C_3H_7COOH	2.9×10^5	3.1	19.6	3.5
n-Valeric, C_4H_9COOH	8.9×10^5	2.7	68.5	3.5
n-Caproic, $C_5H_{11}COOH$	2.4×10^6	3.1	233	2.4
n-Heptylic, $C_6H_{13}COOH$	7.6×10^6	—	555	4.0
n-Octylic, $C_7H_{15}COOH$	—	—	2222	3.2
n-Nonylic, $C_8H_{17}COOH$	—	—	7140	—

this is possible only when the chains are parallel to the surface, i.e., when they lie on it. We will deal with the orientation of surfactant molecules in the surface layer again somewhat later in this section.

The extent to which the Duclaux-Traube rule is observed for the homologous series of fatty acids can be seen from Table 5.4. The rule is observed not only for fatty acids, but also for other homologous series: alcohols, amines, and so forth.

The Duclaux-Traube rule as formulated above is obeyed at temperatures which are close to room temperature. At higher temperatures, the value 3.2 decreases, tending towards unity. This is caused by the fact that, when temperature rises, surface activity diminishes as a result of the desorption of molecules, and the difference between the surface activities of homologues is smoothened out.

The Duclaux-Traube rule is observed only for aqueous solutions of surfactants. In non-polar solvents the solubility of a surfactant increases as the hydrocarbon chain grows, and the surfactant tends to pass over from the surface layer to the volume. Therefore, the Duclaux-Traube rule is reversed.

6. STRUCTURE OF THE ADSORPTION LAYER AT THE SOLUTION—GAS INTERFACE

Above, we have considered adsorption at the solution—gas interface mainly from the thermodynamic point of view. Let us now consider the orientation of surfactant molecules at the solution—gas interface and the structure of the adsorption layer.

To have an idea about the structure of the adsorption layer at the interface, let us consider the results of investigating the structure of films formed when various liquids which dissolve poorly in water are placed on the water surface. A small amount of such a liquid placed on an infinitely large water surface may form a lens-shaped drop if the molecules of the liquid are attracted to one another more strongly than to the molecules of water. Either, the liquid can spread on water, forming a very thin monomolecular layer if the molecules of the liquid are attracted to water more strongly than to one another. Drops are formed when the liquid placed on the water surface is non-polar. The liquid spreads and a monomolecular layer is formed when the molecules are diphilic. Higher fatty acids, alcohols, and amines spread on the surface of water, but almost do not dissolve in it.

Monomolecular films on the water surface can be in three states: gaseous, liquid, and solid. Liquid and solid surface films are known also as condensed films. The state of aggregation of a monomolecular film is determined by the molecular forces which act between the film molecules.

Gaseous surface films. If the forces which act between molecules in a film are comparatively small, the surfactant molecules tend to scatter on the water surface and move away from one another as far as possible, provided the surface is large enough. As a result of thermal motion, molecules always move on the water surface independently of one another, and this causes surface pressure which acts in the direction opposite to surface tension. There is good reason

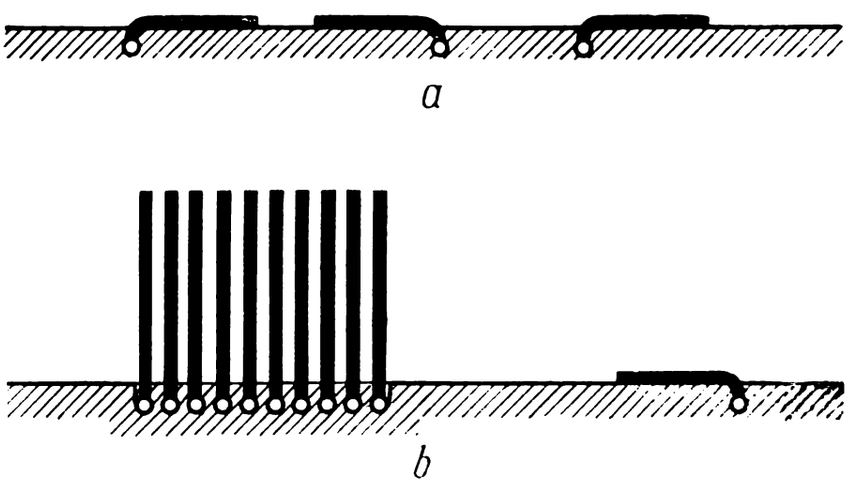


Fig. 5.4. Orientation of molecules of surfactants in the adsorption layer: *a*—two-dimensional gas; *b*—condensed film

to regard such a film* as a two-dimensional gas because the molecules of this gas cannot tear away from water and are forced to move only in two dimensions.

The polar group of the diphilic surfactant molecule will be submerged in water owing to its hydrophilic nature and the ability to be hydrated while the hydrocarbon radical will lie "prostrate" on water because attractive forces operate between the radical and water molecules. The non-polar radical is forced out to the surface not by repulsion which operates between the radical and water molecules, but due to the fact that attraction between water molecules is greater than that between water molecules and the radical.

The orientation of molecules of a two-dimensional gas on the water surface is schematically illustrated in Fig. 5.4*a*.

Substances forming gaseous films on water are organic compounds with diphilic molecules that have a hydrocarbon radical which is not too large and not too small. Such are fatty acids whose chain has carbon atoms that total not less than 12 and not more than 20-22, aliphatic alcohols, and amines whose molecular weight is not too large.

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* The term "film" is not accurate enough. In fact, the molecules of a two-dimensional gas do not form a continuous film on the water surface, but are in thermal motion similar to that of the molecules of a three-dimensional (ordinary) gas. Such films are sometimes called surfactant layers, but this term is also not quite accurate.

The analogy between three-dimensional and two-dimensional gases is not confined to the existence of gas pressure in either case; the equation of state of the same form can be applied to both gases. This can be shown by the following example.

If the surfactant content of a system is small, i.e., if a two-dimensional gas is on the liquid surface, we can write

$$\sigma_0 - \sigma = \Delta = kc$$

Differentiating this equation, we find

$$-d\sigma = d\Delta = k\,dc \tag{5.23}$$

Substituting Eq. (5.23) in Gibbs' equation (5.1) we obtain

$$\Gamma = -\frac{c}{RT}\,\frac{d\sigma}{dc} = \frac{c\,d\Delta}{RT\,dc} = \frac{ck\,dc}{RT\,dc} = \frac{\Delta}{RT} \tag{5.24}$$

Let us denote by ω the area occupied by one mole of a surfactant in the form of a two-dimensional gas. Then,

$$\Gamma = 1/\omega$$

Substituting this value of Γ in Eq. (5.24), we get:

$$1/\omega = \Delta/RT \tag{5.25}$$

or

$$\Delta\omega = RT \tag{5.26}$$

This equation is similar to the Mendeleyev-Clapeyron equation per mole of a gas:

$$pV = RT$$

Indeed, in the Mendeleyev-Clapeyron equation, V is the volume of a three-dimensional gas, and in Eq. (5.26), ω is the "volume" of a two-dimensional gas, its surface area. In the Mendeleyev-Clapeyron equation, p is pressure, whereas in Eq. (5.26), Δ is the diminution of surface tension as a result of the action of surface pressure, i.e., a quantity that is equal to the pressure of a two-dimensional gas.

The state of a real three-dimensional gas is described by the well-known van der Waals equation

$$(p + a/V^2)\,(V - b) = RT$$

As A. Frumkin has shown, a similar equation must be used for a two-dimensional gas under the appropriate conditions:

$$(\Delta + \alpha/\omega^2)\,(\omega - \beta) = RT \tag{5.27}$$

In Eq. (5.27), the quantities α and β correspond to the constants a and b in the van der Waals equation. In this case, the correction α/ω^2, determined by the existence of forces of attraction between

the hydrocarbon radicals of molecules, begins to have an effect only when the radicals are sufficiently long.

Condensed (liquid and solid) films. If the tangentially acting forces between the hydrocarbon radicals of surfactant molecules in the surface film are great, the molecules stick together and form large condensed "islands" in which the thermal motion of molecules is considerably hindered. In such "islands", molecules are oriented parallel to one another and perpendicular to the water surface, forming a "palisade". In fact, according to some authors, molecules of such a film can be oriented also at an angle to the surface. Of course, molecules may tear away from these "islands" and fill the surface between them as a rarefied gaseous film. Such a phenomenon is similar to the evaporation of a liquid or the sublimation of a solid. The structure of condensed films is schematically illustrated in Fig. 5.4*b*.

Substances which form condensed films in water under ordinary conditions are organic compounds with diphilic molecules that have long hydrocarbon radicals because the elongation of a chain increases the interaction between molecules. When conditions are changed, e.g., when temperature rises, condensed surface films are capable of becoming gaseous films in many cases.

Condensed films are usually liquid, and molecules in them move rather freely. However, condensed films can be regarded as solid ones if the forces acting between the radicals of molecules are so great that the molecules cannot move. This occurs when the hydrocarbon radicals of diphilic molecules contain more than 20-24 carbon atoms, i.e., they are quite long. The fact that condensed films possess properties of a solid can be verified by depositing a light powder on them. If the film is solid, the powder does not move when one carefully blows on it. If the film is liquid, the powder moves along the surface. Another method of determining the state of aggregation of a film is by immersing a small glass disc, which is suspended by a quartz thread attached to a horizontally pivoted head, half into a liquid. If the film is solid, a certain angle of torsion is formed as the head rotates; only then the disc tears the film and follows the head. If the film is liquid, the disc follows the twirling head without forming the angle of torsion.

Besides the types of films described above, there are *expanded* films which by their properties hold an intermediate place between gaseous and condensed films. Such films are formed, for example, from condensed films when temperature rises. In a certain temperature range, condensed films expand and then the area occupied by a film no longer depends on temperature. It is assumed that hydrocarbon chains of molecules in expanded films are not parallel to one another. Instead, they are interlaced to a certain extent or, at least, they energetically interact with one another, lying flat

on water, and this prevents the film from spreading infinitely. The polar groups of molecules in such films move rather freely in the water layer that is near the surface. Measurements made by Langmuir's balance (which is described below) have shown that, in expanded films, the area occupied by a molecule has an intermediate value between the areas of molecules oriented along the normal to the water surface and those lying flat on it.

Expanded films are formed because the kinetic energy of the hydrocarbon radicals of molecules which form a condensed film increases as temperature rises. The same diminution in the length of the hydrocarbon chain always corresponds to the same decrease in temperature at which the film expands. At the same time, this temperature does not depend on the nature of a polar group. The ability to form expanded films grows when there is a double bond at the centre of the aliphatic radical of a diphilic molecule; this is apparently due to the great attraction of the double bond to water. Experiment has also shown that the ability of a surface film to be in the expanded state is affected by the state of polar groups. For example, fatty acids at definite temperatures form expanded films on neutral and acidic solutions, i.e., when polar groups are almost undissociated. On alkaline solutions, fatty acids produce gaseous films under the same conditions because the like charges of neighbouring polar groups which have appeared as a result of their dissociation are repelled.

7. LANGMUIR'S BALANCE. DETERMINATION OF THE DIMENSIONS OF SURFACTANT MOLECULES

Langmuir brilliantly proved the existence of gaseous and condensed surface films by means of a special balance which he made himself; this balance makes it possible to determine the surface pressure that acts on a film and to establish the dependence of this pressure on the area occupied by the film.

The design of Langmuir s balance as it was first constructed is shown in Fig. 5.5.

Measurement by means of such a balance is made in the following way. A small amount of a volatile solvent containing an insoluble substance capable of forming a surface film is placed on the surface of water which is poured to the level of the edges of cuvette *1* and confined on the left and right by barriers *2* and *3* made of strips of paper impregnated with paraffin. The solvent rapidly evaporates and diphilic molecules of the substance spread on the water surface. The space occupied by the film is reduced by bringing the left movable barrier *2* closer to the right barrier *3* which is connected to beam *4*. Barrier *3* moves to the right under the action of greater surface pressure of the film and thus puts beam *4* connected to it out of equi-

librium. The balance can be brought to the zero position by putting weights on pan *5*. Thus, the pressure acting on the film can be measured.

After performing this operation several times, we can obtain data for plotting the isotherm which connects the pressure acting on the film with the area occupied by a known amount of the test substance

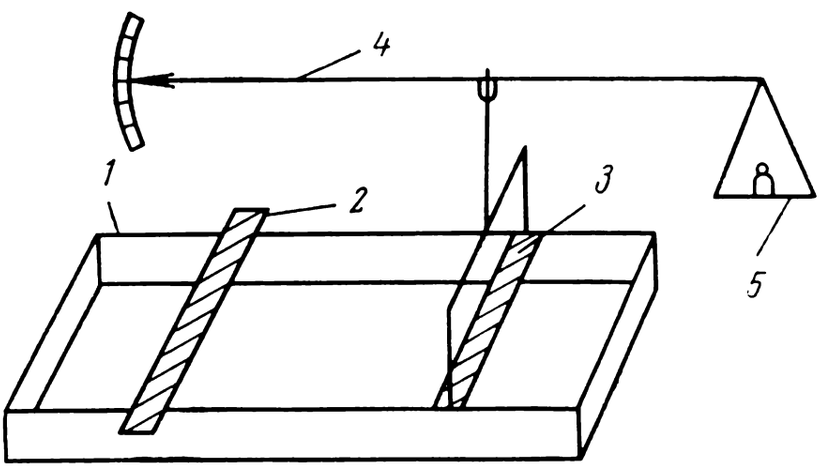

Fig. 5.5. Langmuir's balance:
1—cuvette; *2*, *3*—left and right barriers; *4*—beam; *5*—pan

or with the area occupied by one molecule of the substance. The latter can be easily calculated if the area occupied by the substance, its mass, and molecular weight are known.

Figure 5.6 shows the isotherms obtained by Adam for various fatty acids at 12.5-14.5 °C. Curve *1* is for lauric acid ($C_{11}H_{23}COOH$) which forms only gaseous surface films owing to the comparatively short hydrocarbon radical. The shape of this isotherm is similar to that of the isotherm $pV = \text{const}$ for an ideal three-dimensional gas.

Curve *2* was obtained for myristic acid ($C_{13}H_{27}COOH$) which is capable of producing both gaseous and condensed films. In this case, after a certain degree of compression of the film (a definite area per molecule) is attained, pressure ceases to increase and the curve is parallel to the abscissa at a certain region. This region which is similar to the region of the isotherm p, V for a real three-dimensional gas indicates the condensation of a two-dimensional gas and corresponds to the equilibrium between two surface phases: the gaseous film and islets of the condensed film.

The observed maximum pressure (about 0.4 dyn/cm) of a two-dimensional gas during its condensation may seem to be very small. But this is not so. The molecules of a two-dimensional gas lie flat and the thickness of the surface film is only about 4.5 Å. The surface pressure of 0.4 dyn/cm corresponds to approximately 8.7×10^6 dyn/cm^2, or 8.5 atm. This value is rather close to that of critical pressure for ordinary liquids.

As the film is compressed further, the "islets" come against one another and the two-dimensional gas between them disappears, and then pressure grows sharply again. Lastly, when pressure is comparatively high, it attains a definite limit and does not change any more (this region is not indicated in Fig. 5.6). This limit corresponds to the pressure at which the film disintegrates. In this case, separate fragments of the film get on top of one another, like blocks of ice as they flow, and then a polymolecular surfactant layer is formed on the water surface.

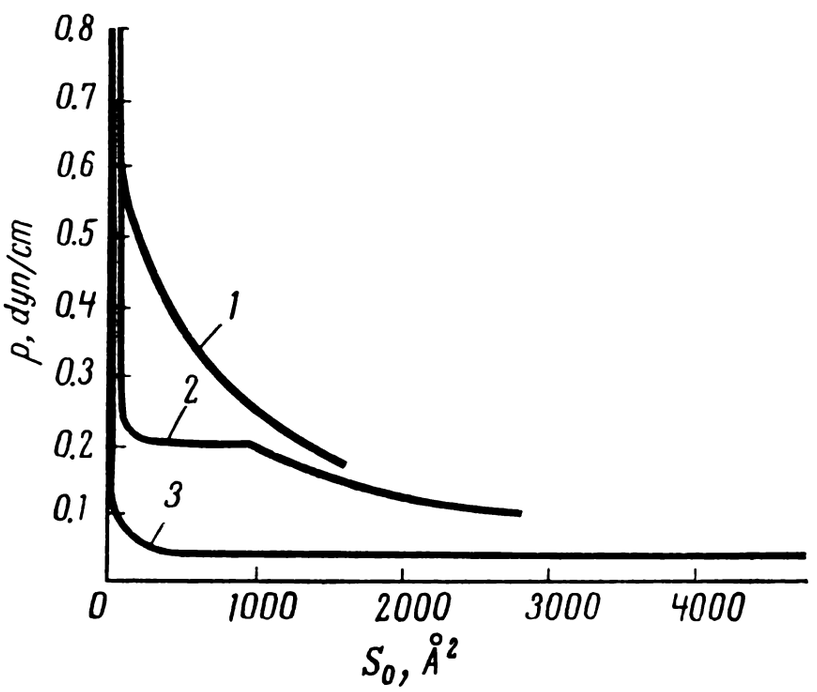

Fig. 5.6. Dependence of surface pressure p on the area s_0 occupied by an acid molecule:

1—isotherm for lauric acid; *2*—the same for myristic acid; *3*—the same for palmitic acid

Curve *3* is for palmitic acid ($C_{15}H_{31}COOH$) which has a high molecular weight. This acid forms only condensed films at ordinary temperature owing to the strong interaction between long hydrocarbon radicals. If such a film is given a sufficiently large surface, a two-dimensional gas covers the remaining surface of the liquid not occupied by the film, but the pressure of this gas is so small that it is difficult to be measured. When such films are sufficiently compressed, the pressure suddenly rises, implying that the entire water surface is covered with a condensed film. When the film is compressed further, it disintegrates in a similar way as the film of myristic acid.

When a dependence is established between surface pressure and the area occupied by a molecule, it is possible to not only find a connection between the nature of a surfactant and that of the film being formed, but also ascertain the effect of temperature on the film structure. Experiments have shown that, as temperature rises, the molecular forces between the hydrocarbon radicals are at first overcome in the film which first expands and then becomes gaseous.

All we have said about the orientation of surfactant molecules at the water—air interface has related to films obtained from diphilic molecules which are poorly soluble in water. However, this also relates to surface films of soluble substances which are formed upon adsorption of their molecules. A certain equilibrium is always established between the amount of a substance on the surface and that in the volume. Moreover, the surface films of soluble surfactants are almost always gaseous owing to the comparatively small length of the hydrocarbon radicals of their molecules.

The dimensions and shape of the molecules forming a film can be determined from the dependence of surface pressure on the area of a film in the cuvette of Langmuir's balance. In some cases, such investigations made it possible to specify the structure of molecules which hitherto had remained unclear. It is precisely by means of this method that the structure of some esters of high molecular weight alcohols and other organic compounds has been ascertained.

Let us consider how the given technique can be used to determine the dimensions and shape of diphilic molecules of water insoluble substances. A sharp rise in the isotherm for pressure and film area corresponds to the formation of a closely packed layer of molecules that are perpendicular to the water surface. The relevant inflection of the curve makes it possible to find the area s_0 per molecule which is normal to the water plane:

$$s_0 = \frac{s}{N_A m/M} = \frac{1}{N_A m/Ms} = \frac{1}{\Gamma_{max} N_A} \qquad (5.28)$$

where s = area of the film equal to the product of the distance between barriers by the width of the cuvette of Langmuir's balance;
m = mass of a substance taken for a determination;
M = molecular weight of a substance;
N_A = Avogadro number.

The value of s_0 found by this method for all the fatty acids having 14 or more carbon atoms in a chain is 20.5 Å^2. The fact that the area occupied by a molecule in a continuous monomolecular layer does not depend on the chain length confirms the arrangement of molecular chains which do not lie on the water surface but are oriented more or less vertically. X-ray analysis has shown that the sectional area of parallel, closely packed hydrocarbon chains in crystals is 18.4 Å^2. This is quite close to the value of 20.5 Å^2. The values of s_0 for molecules of fatty acids in films are somewhat higher because either their packing density is smaller or they are not quite perpendicular to the surface but form a certain angle with it.

Experiments have also shown that s_0 does not change with an increase in the length of the hydrocarbon radical but depends on the

polar group of a molecule. For example, s_0 for fatty acids is 20.5 Å^2; for esters of saturated acids, 22 Å^2, for alcohols, 21.6 Å^2. This indicates that s_0 is a molecular constant which characterizes the polar group of a diphilic molecule. Moreover, s_0 depends very little on the nature of surface on which a film was formed. For example, the area occupied by a molecule of *p*-toluidine at the interface between an aqueous solution and air is 25.4 Å^2; at the water—hexane interface, 26.2 Å^2; at the water—benzene interface, 25.8 Å^2. Therefore, when the value of Γ_{max} and n, the number of moles of a substance adsorbed by a surface under conditions which conform to the formation of a continuous monomolecular layer, are known, the adsorbent surface s can be calculated by using the simple equation

$$s = n_{max}/\Gamma_{max} \tag{5.29}$$

This method is widely used for determining the specific surface area of various adsorbents and disperse systems, employing the equation

$$s_{sp} = s/m \tag{5.30}$$

The thickness δ of the surface film or, what is the same, the length of a molecule of a substance when its arrangement on the surface is assumed to be vertical, can likewise be calculated. The volume of the surface layer per unit surface is apparently numerically equal to δ. On the other hand, the volume of this layer is equal to $\Gamma_{max}V_{mol}$ (where V_{mol} is the molar volume). Therefore,

$$\delta = \Gamma_{max}V_{mol} = \Gamma_{max}M/\rho \tag{5.31}$$

where ρ is the density of the adsorbed substance.

The value of δ in a homologous series should grow regularly with the chain length. Indeed, it was found that, when the aliphatic chain is elongated by the CH_2 group, δ grows by 1.43 Å. It has been established by X-ray analysis that the distance between two carbon atoms in the hydrocarbon chain, where valency bonds are arranged at an angle of 109°28′, is 1.54 Å, and between the carbon atom of the main chain and the carbon of the side chain, 1.26 Å.

The last value does not coincide with the value of 1.43 Å apparently owing to the same reasons why the values of s_0 determined by Langmuir's balance and by X-ray analysis do not coincide.

6

ADSORPTION AT THE SOLID—SOLUTION INTERFACE

Adsorption from a solution on a solid surface is probably the most important to colloid chemistry because this adsorption is precisely the basis of such important phenomena as the formation, stability, and disintegration of lyosols.

Adsorption at the solid—solution interface is in general similar to that at the solid—gas interface, but in the former case the phenomenon is complicated by the presence of a third component, i.e., the medium (solvent) whose molecules may also be adsorbed on the adsorbent surface and thus compete with the adsorptive molecules. Hence, this type of adsorption is always adsorption from a mixture. Moreover, adsorption at the solid—solution interface is always complicated by the interaction between the adsorptive molecules and the molecules of the medium.

In considering adsorption from a solution on a solid, two cases should be distinguished: adsorption of non-electrolytes when the adsorptive molecules are adsorbed, and the adsorption of electrolytes when one of the ions of an electrolyte is selectively adsorbed.

1. MOLECULAR ADSORPTION FROM SOLUTIONS

The amount of a substance a molecularly adsorbed by one gram of an adsorbent from a solution is usually calculated by the equation

$$a = \frac{(c_0 - c_1)\,V}{m}\,1000 \qquad (6.1)$$

where c_0 and c_1 = initial and equilibrium concentrations of the adsorptive, mol/l;
V = volume of the solution from which adsorption occurs, l;
m = mass of the adsorbent, g;
1000 = conversion factor (for converting the quantity being measured into mmol/g).

Sometimes, when the specific area of the adsorbent is known, the quantity of adsorption is related to unit surface (usually to one square centimetre).

The effect of the concentration of the adsorptive on the molecular equilibrium adsorption from a solution on a solid is characterized by an ordinary isotherm of adsorption; for sufficiently diluted solutions, adsorption in this case is described well by Freundlich's empirical equation (4.2) or Langmuir's equation (4.10). Gibbs' equation can be used for describing adsorption from a solution on a solid only indirectly owing to the complexity of determining surface tension at the solid—solution interface.

Nevertheless, the quantity of Gibbs' adsorption can be easily determined experimentally by measuring the change in the molar concentration of the adsorptive in a solution as a result of adsorption. If the total number of moles of a substance in a solution is equal to n, and the molar fraction of the adsorptive in the solution before adsorption was N_0 and constituted N when equilibrium was established with the adsorbent, then

$$\Gamma = \frac{n'(N_0 - N)}{m \cdot s_{sp}} \tag{6.2}$$

where m = mass of the adsorbent;
s_{sp} = specific surface area of the adsorbent.

Effect of the nature of the medium. The molecules of the adsorptive and of the medium compete during adsorption from a solution; apparently, the worse a medium is adsorbed on an adsorbent, the better is the adsorption of a dissolved substance. Since surfactants have low surface tension, it may be assumed that the higher the surface tension of the medium, the less is the adsorbability of its molecules on a solid and the better is a dissolved substance adsorbed on it. That is precisely why adsorption on a solid usually occurs better from aqueous solutions but worse from solutions in hydrocarbons, alcohols, and other organic liquids having comparatively small surface tension.

Another criterion of the usefulness of a solvent as a medium for adsorption is the heat of immersion of the adsorbent by the solvent. When an adsorbent is immersed in a liquid, the heat of immersion Q is liberated, which is equal to the difference of the total surface energies of the adsorbent*

$$Q = s_{sp}(E_1 - E_2) \tag{6.3}$$

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* The total energy E per unit surface area is the sum of the free surface energy σ and bound energy Q_s. The quantity Q_s is heat required for maintaining constant temperature when the surface expands isothermally per unit area.

where s_{sp} = specific surface area of the adsorbent;
E_1 and E_2 = total surface energy at the adsorbent—air and adsorbent—liquid interfaces, respectively.

The difference in the polarities of surfaces on the second interface is always smaller than that on the first; therefore, $E_1 > E_2$ and $Q > 0$. The heat of immersion is usually in the range of 1-20 cal per 1 g of the adsorbent; it depends on the values of E_1 and E_2 and on the porosity or degree of dispersion of the adsorbent.

The more is heat liberated in wetting, the more intensive is the energetic interaction between the solvent and the adsorbent and, consequently, the worse is a given liquid as a medium for adsorption. This principle is supported by the data of Table 6.1 which gives the values of the heats of immersion for floridin and various solvents, and the amount of benzoic acid adsorbed by floridin from these solvents.

Table 6.1. **Adsorption of Benzoic Acid on Floridin from 1 Per Cent Solutions**

Solvent	Heat of immersion, cal/g	Amount of adsorbed acid, mmol/g
Acetone	27.3	0
Ethyl acetate	18.5	0.22
Chloroform	8.4	3.50
Benzene	5.6	3.64
Carbon tetrachloride	4.6	3.95
Ligroin (fraction in the range of 60-80 °C)	4.2	4.01

Substances consisting of polar molecules produce a great thermal effect when they are wetted by polar liquids (e.g., water); substances consisting of non-polar molecules liberate more heat when they are wetted by non-polar liquids (e.g., hydrocarbons). Since the heat of immersion is strongly affected by the specific area, P. Rehbinder proposed the quantity α, i.e., the ratio between the heat of immersion of a powder by water (Q_1) and by a hydrocarbon (Q_2), as a criterion of interaction between the polar medium (water) and the adsorbent:

$$\alpha = Q_1/Q_2 \tag{6.4}$$

The dielectric constant is to a certain extent a measure of polarity of a substance; consequently, there is a certain connection between the dielectric constant of liquids, on the one hand, and the adsorbability of various adsorptives in these liquids, on the other.

As a first approximation, we can also assume that the better a medium dissolves an adsorptive, the worse is adsorption in the me-

dium. This principle is one of the reasons for reversing the Duclaux-Traube rule. For example, when a fatty acid is adsorbed on a hydrophilic adsorbent (e.g., silica gel) from a hydrocarbon medium (e.g., benzene), adsorption does not increase with the molecular weight of the acid as should be expected according to the Duclaux-Traube rule, but decreases because higher fatty acids dissolve better in a non-polar medium.

Effect of the properties of the adsorbent and the adsorptive. Adsorption from solutions is strongly affected by the polarity and porosity of the adsorbent. Non-polar adsorbents adsorb non-polar adsorptives better, as a rule, while polar adsorbents adsorb better polar adsorptives.

The effect of adsorbent porosity depends on the relationship between the dimensions of adsorbent pores and of adsorptive molecules. As adsorbent porosity increases, the adsorption of small molecules from solutions usually grows because fine-pored adsorbents have great selective action, and the effect of the chemical nature of their surface is higher. However, this dependence is valid only when adsorptive molecules are sufficiently small and can readily penetrate into pores. Large adsorptive molecules cannot get into narrow adsorbent pores, and adsorption decreases or, in any case, is much retarded. This may also result in the reversion of the Duclaux-Traube rule, i.e., adsorption on adsorbents having narrow pores decreases rather than increases, as adsorptive molecules become larger. Table 6.2 gives data which characterize this principle; the coefficient β from Freundlich's equation is taken for characterizing adsorbability.

Table 6.2. **Adsorption of Fatty Acids from Aqueous Solutions on an Adsorbent Having Narrow Pores**

Acid	Number of carbon atoms in a chain	Coefficient β
Formic	0	0.546
Acetic	1	0.238
Propionic	2	0.111
Butyric	3	0.056
Valeric	4	0.032
Caproic	5	0.020

Of course, the Duclaux-Traube rule cannot be reversed for non-porous adsorbents having a smooth surface.

In considering the effect of the chemical nature of an adsorptive on its adsorbability on a solid, it is difficult to make any generali-

zations because the adsorbability of the same adsorptive greatly depends on the polarity of the adsorbent and the medium. Nevertheless, in determining the effect of the properties of the adsorptive on adsorption, the rule of polarity equalization formulated by Rehbinder may be used. According to this rule, substance C can be adsorbed at the interface of phases A and B if the presence of substance C in the surface layer equalizes the difference in the polarities of these phases. In other words, adsorption will occur if the value of polarity of substance C, characterized, for example, by the dielectric constant ε, is between the values of polarities of substances A and B, i.e., if the following condition is met:

$$\varepsilon_A > \varepsilon_C > \varepsilon_B \text{ or } \varepsilon_A < \varepsilon_C < \varepsilon_B$$

It also follows from the rule of polarity equalization that the greater the difference in polarities between the solute and the solution, i.e., the smaller the solubility of a substance, the better is it adsorbed.

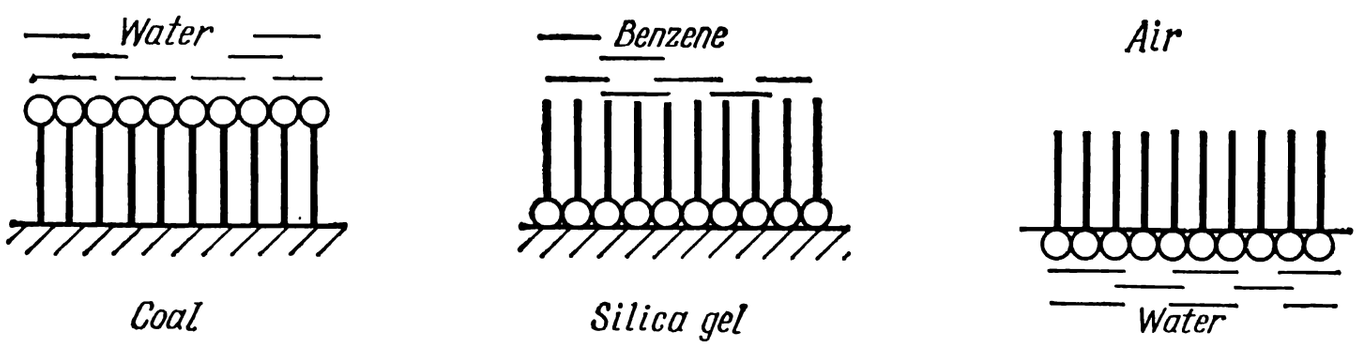

Fig. 6.1. Diagram of the orientation of diphilic molecules at the interface of a different nature

Moreover, according to Rehbinder's rule, diphilic surfactant molecules should orient at the adsorbent—medium interface so that the polar part of the molecule faces the polar phase while the non-polar part faces the non-polar phase. If air is one of the phases, it can be regarded as a non-polar phase. The orientation of molecules of diphilic substances, e.g., molecules of a fatty acid, at the interfaces of different phases is schematically illustrated in Fig. 6.1.

The conclusion can thus be drawn that all the polar hydrophilic surfaces adsorb well the surfactants from non-polar or weakly polar liquids and, conversely, the non-polar hydrophobic surfaces adsorb well the surfactants from polar liquids (e.g. aqueous solutions). This is precisely why polar adsorbents (silica gel, clays, floridin) are used for the adsorption of surfactants from non-polar media, and non-polar adsorbents (coal) for the adsorption from polar media.

There are several particular rules apart from the general principles concerning the effect of the nature of an adsorptive on adsorption. For example, the adsorbability of a substance increases with its

molecular weight. That is why alkaloids and also dyes which usually have high molecular weights are adsorbed well. Aromatic compounds are, in general, adsorbed better than aliphatic ones, and unsaturated compounds are adsorbed better than saturated ones. Traube's rule is obeyed qualitatively in the adsorption of fatty acids and alcohols on solids, as well as during the adsorption at the solution—air interface.

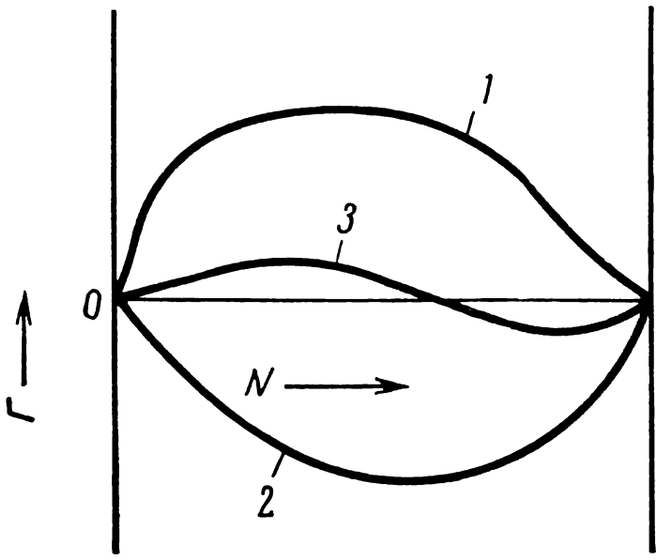

Fig. 6.2. Dependence of Γ on the molar fraction N of the adsorptive: *1*—strong adsorption of the adsorptive and weak adsorption of the solvent; *2*—weak adsorption of the adsorptive and strong adsorption of the solvent; *3*—weak adsorption of the adsorptive and the solvent

Effect of time, temperature, and the concentration of a solution. The adsorption of a solute occurs more slowly than that of a gas because a decrease of the concentration in the boundary layer can be restored only by diffusion which is generally rather slow in a liquid. To establish adsorption equilibrium more rapidly, the system is often stirred.

Large molecules on an adsorbent having sufficiently narrow capillaries are adsorbed particularly slowly. Under these conditions either equilibrium is established extremely slowly or it is not established at all. Table 6.3 presents data characterizing the rate of adsorption of two fatty acids of different molecular weights on charcoal having pores of different diameters. As we may see, the establishment of adsorption equilibrium takes a longer time as the molecular weight of an acid increases.

Table 6.3. **Dependence of the Time Required for Establishing Adsorption Equilibrium on the Dimensions of Molecules of Fatty Acids and the Dimensions of Charcoal Pores**

Characteristics of pores	Time required for establishing adsorption equilibrium for	
	propionic acid	heptylic acid
Comparatively large	<1 hour	2 hours
Have an average diameter	3 days	~ 32 days
Narrow	10 days	Equilibrium is hardly established
Very narrow	>30 days	Ditto

As temperature rises, adsorption from a solution decreases but usually to a smaller extent than the adsorption of gases. However, when the solubility of a poorly soluble adsorptive in a solvent increases with temperature, adsorption can also grow owing to considerably high concentrations of the equilibrium solution. Such a phenomenon is observed, for example, in the adsorption of naphthalene on the hydroxylated surface of silica from a solution in *n*-heptane.

Figure 6.2 schematically shows the change in the quantity of Gibbs' adsorption Γ in conformity with the molar fraction N of the adsorptive in the equilibrium solution. When the adsorptive is strongly adsorbed and the solvent is weakly adsorbed, curve *1* at first sharply rises, passes through a maximum, and then drops to zero almost rectilinearly. The value of adsorption Γ diminishes because, at high values of N, the concentrations of the adsorptive in the surface layer and in the volume of the solution become very large and equal. Isotherm *2* characterizes negative adsorption whose absolute value grows linearly at first; it then attains a maximum and finally drops to zero when the concentrations of the adsorptive in the surface layer and in the volume are very high. Isotherm *3* at first characterizes positive Gibbs' adsorption which later changes the sign, passes through zero, and becomes negative. Negative adsorption also attains zero as N increases. At the point where the isotherm intersects the abscissa, the concentrations of the solution on the surface and in the volume are the same, and therefore a given adsorbent cannot be used to separate the mixture. This phenomenon is known as *adsorption azeotropy*.

Adsorption from a solution is determined not by the total value of the potential energy of the system of the adsorptive molecule and the adsorbent as in gas adsorption at low pressure, but by the difference in the potential energies of the adsorptive molecule in respect to the adsorbent and the solvent. Therefore, the heat of adsorption of the adsorptive from the solution is usually several times smaller than that on the same adsorbent from a gaseous phase.

The adsorption of fatty acids and several other surfactants from their solutions in non-polar liquids can cause the formation of boundary polymolecular layers 0.05-0.5 μm thick on the surface of solids. As B. Deryagin, G. Fuchs, and their coworkers have shown, the mechanical properties of such layers differ from those of the volume layers of a solution and depend on the structure and the molecular weight of surfactant molecules. The thickness of the boundary layer of solutions of fatty acids in hexane or benzene is a linear function of the length of the hydrocarbon radical, and the "melting" point of this layer (the diminution of mechanical properties down to the value of the properties of the solution volume) depends on the melting point of the appropriate surfactants. The boundary layers ensure

the stability of disperse systems in non-polar liquids and play an important role in the action of lubricants.

Importance of adsorption from solutions in nature and industry. Adsorption from solutions is important for most physico-chemical processes which occur in plants and animals. Chemical transformations involved in the assimilation of nutrients begin with the accumulation of reactants on the surface of natural catalysts, i.e., enzymes. The penetration of substances into an organism through semipermeable membranes also begins with adsorption at the interface.

Molecular adsorption from solutions is widely used in industry. T. Lowitz was the first to use adsorption as early as the 18th century for purifying solutions by charcoal in order to remove various impurities. At present, sugar syrups are usually clarified by treating them with activated charcoal. Lubricants are also purified by special clays which act as an adsorbent.

Adsorption is used to extract small amounts of substances dissolved in large volumes of liquids, for example, in the processing of rare elements.

Adsorption is widely used in analytical chemistry for separating compounds which otherwise are difficult to separate. Adsorption processes are the basis of chromatography which was first used by the Russian scientist M. Tswett in 1903 to separate a mixture of plant pigments into constituents.

Adsorption chromatography in its simplest form consists in the slow passage of a mixture of dissolved substances to be separated for a long time through a tube (adsorption column) that is filled with an adsorbent (Al_2O_3, MgO, CaO, $CaCO_3$, Fuller's earth, floridin). Components which adsorb better are bound to the adsorbent in the upper part of the column. Components which are adsorbed to a lesser extent are bound in the middle of the column. Components of the least adsorbability are bound to the adsorbent only at the bottom of the column because they are forced from the upper adsorbent layers by substances which adsorb better as new portions of solutions pass through these layers.

As a result, zones saturated with components of a mixture are formed along the height of the adsorbent column. If the components have a different colour, the zones can be easily distinguished by their colour. If the components are colourless but luminesce, the adsorbent layer is investigated in ultraviolet light to determine the boundaries between the zones.

To isolate components of a mixture, the column is carefully pressed out of the tube and cut into short columns (zones) from which the adsorbed component can then be extracted with a suitable solvent.

Figure 6.3 shows a chromatogram of chlorophyll consisting of several substances which have a similar structure but differ in colour.

Therefore, we cannot divide them by chemical methods, but can distinguish them by colour, using chromatography.

To make the boundary between separate zones in which the adsorption of substances is more pronounced, the chromatogram must be "developed" further. To this end, a comparatively small amount of the test mixture dissolved in a suitable solvent is passed through the column. Then, a pure solvent (or several solvents consecutively) is passed through the column, and the eluate, in which the components appear one after another as their adsorbability grows, is investigated. This is known as the developing method. Fig. 6.4 shows a typical differential chromatogram which is obtained when a mixture of amino acids is separated on a starch column. Almost every component produces an independent peak and can be collected as a separate fraction.

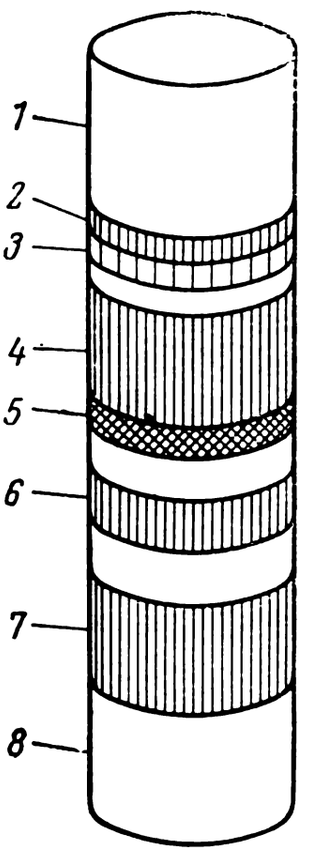

Fig. 6.3. Chromatogram of plant pigments:
1—colourless layer; *2*—xanthophyll β (yellow); *3*—chlorophyllin β (yellow-green); *4*—chlorophyllin α (green-blue); *5*—xanthophyll β′ (yellow); *6*—xanthophyll α′ (yellow); *7*—xanthophyll α (yellow); *8*—chlorophyllin (steel-grey)

Instead of a solvent, a solution of a substance which is adsorbed better than any component of the test mixture may be passed through the column. The chromatogram then also has several peaks arranged according to the increasing adsorbability of substances, and it ends with the outlet of the pure extruding substance. This chromatographic method is known as the extrusion method.

We have dealt briefly with some methods of liquid chromatography. However, there are many other chromatographic techniques: precipitation, gas, gas-liquid, thin-layer chromatography, and so forth. All these methods are considered in detail in special sections of analytical chemistry.

In chromatography, the initial act of adsorption can have the nature of molecular adsorption or ion exchange, depending on the adsorbent and the substances being separated. The initial processes of molecular adsorption in chromatography obey Langmuir's or Freundlich's equation; the initial processes in ion exchange obey Nikolsky's equation which will be considered below.

Chromatography is widely used in separating and purifying medicinals, vitamins, pigments, enzymes and other proteins, and alkaloids.

Chromatography has been important in the discovery of new, artificially prepared transuranic elements. It is precisely by means

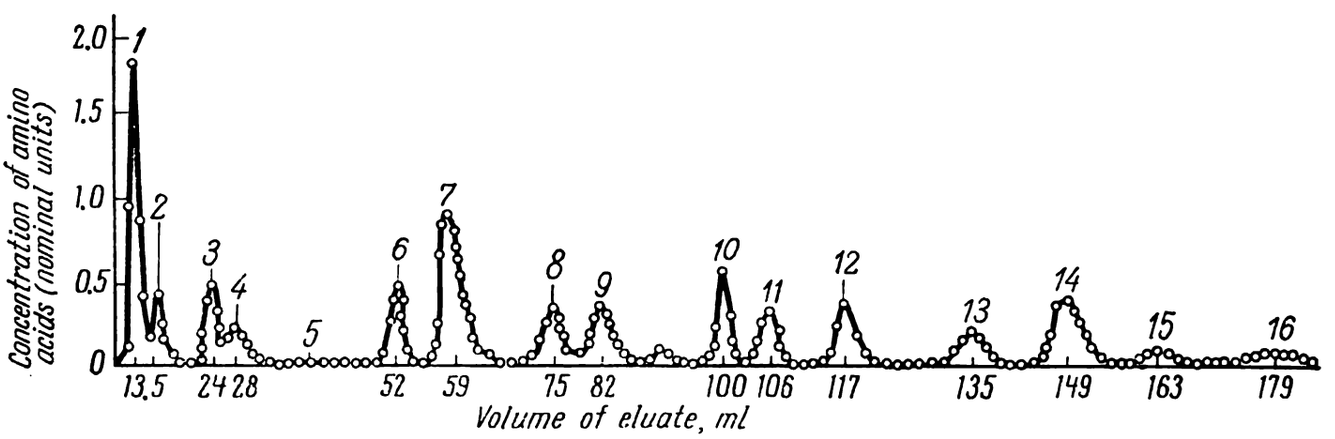

Fig. 6.4. Elution of amino acids after chromatography on a starch column (according to Stein and Moore); solvents: *n*-butanol, *n*-propanol, 0.1 N HCl (1 : 2 : 1); after aspartic acid: *n*-propanol, 0.5 N HCl (2 : 1)

amino acids: *1*—leucine + isoleucine; *2*—phenylalanine; *3*—valine; *4*—methionine; *5*—tyrosine; *6*—proline; *7*—alanine + glutamic acid; *8*—threonine; *9*—aspartic acid; *10*—serine; *11*—glycine; *12*—ammonia; *13*—arginine; *14*—lysine; *15*—histidine; *16*—cystine

of this method that the elements No. 99 Einsteinium (Es), No. 100 Fermium (Fm), and No. 101 Mendelevium (Md) have been separated.

2. IONIC ADSORPTION

The adsorption of electrolytes is not within the scope of the science of molecular adsorption; it requires special consideration because the adsorbent can variously adsorb ions into which a molecule of an electrolyte disintegrates in a solution. Since aqueous electrolytic solutions are of the greatest practical importance, let us consider only the adsorption of electrolytes from such solutions.

Ionic adsorption is considerably affected by the nature of the adsorbent. Ions capable of being polarized are adsorbed on surfaces that consist of polar molecules or ions. Therefore, ionic adsorption is often called *polar adsorption*. The microregions of a surface bearing a definite charge adsorb oppositely charged ions. Electrolytic ions of opposite sign are not adsorbed directly here but remain near the adsorbed ions, under the action of the forces of electrostatic attraction, forming the *electric double layer* with them on the adsorbent surface. The structure of this layer is considered in detail in Chap. 7, which treats the electrical properties of colloidal particles.

The radius of ions strongly affects their adsorbability. Among ions of the same valency, ions of the largest radius exhibit maximum ad-

sorbability, because, on the one hand, such ions are greatly polarizable and, consequently, they are capable of being attracted by the surface which consists of ions or polar molecules; on the other hand, these ions are hydrated to a smaller extent (the larger the radius of an ion, the smaller is its hydration when the charge is the same). Hydration in general hinders ionic adsorption because a hydrate shell reduces electric interaction.

The difference in the hydration of monovalent cations is schematically illustrated in Fig. 6.5. The solid line denotes the boundary

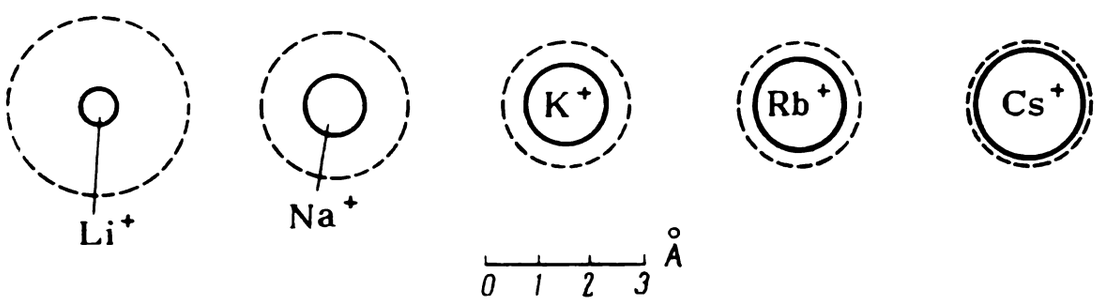

Fig. 6.5. True radii of monovalent cations and their radii in a hydrated state

of the ion, and the dotted line, the boundary of its hydrate shell. The scheme shows that the lithium ion is much more hydrated than the cesium ion. The series of ions composed according to their ability to interact with the medium are known as the *lyotropic series* or the *Hofmeister series.* Monovalent cations can be put in the following series according to their adsorbability:

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

Bivalent cations will have the following series:

$$Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$$

Monovalent anions are arranged in the following sequence according to the growth of their adsorbability:

$$Cl^- < Br^- < NO_3^- < I^- < NCS^-$$

The adsorbability of ions also greatly depends on their valency. The higher the valency of an ion, the stronger is it attracted by the oppositely charged microregions of a surface. Cations of a different valency can be arranged in the following series according to the growth of their adsorbability:

$$K^+ \ll Ca^{2+} \ll Al^{3+} \ll Th^{4+}$$

The adsorption of ions by the surface of a crystal whose composition includes ions of the same nature is especially interesting to colloid chemistry. In this case, adsorption can be regarded as crystallization, i.e., as the completion of a crystal lattice by an ion which is capable of being adsorbed. According to F. Paneth and K. Fajans, the construction of crystals is completed only by the ions and atoms that are in their composition. For example, AgI

crystals introduced into a solution of KI adsorb iodide ions on the surface. If AgI crystals are introduced into a solution of $AgNO_3$, silver ions are adsorbed. Of course, the forces under whose action such a construction is finished are chemical and, at the same time, electrostatic forces, and the ions which complete the construction of crystals are adsorbed here especially firmly. Figure 6.6 schematically

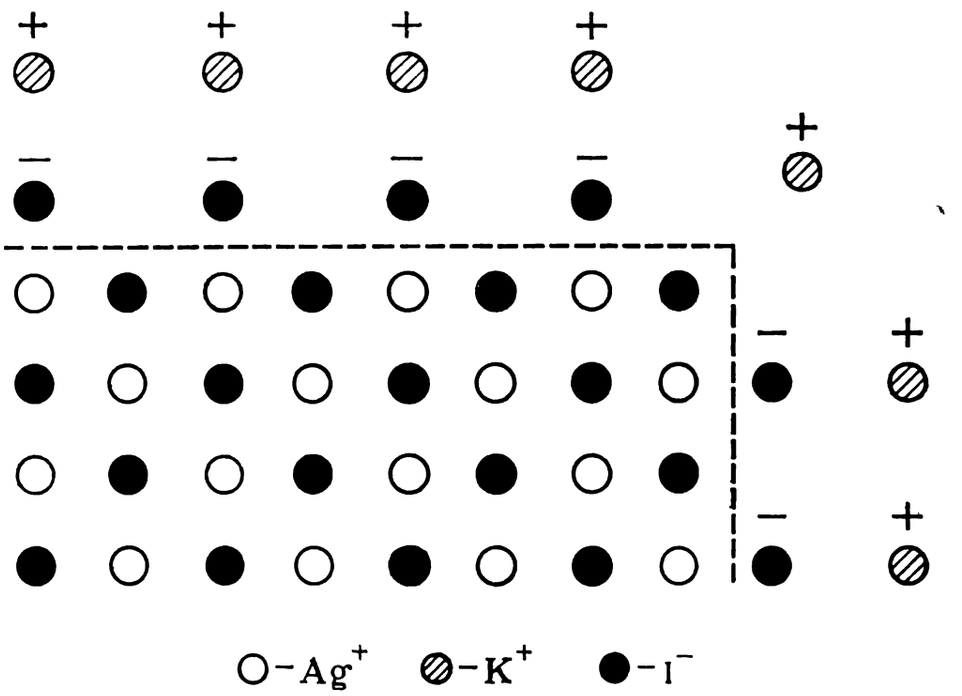

Fig. 6.6. Finished construction of a crystal of silver iodide in a solution of potassium iodide

shows the finished construction of a crystal of silver iodide in a solution of potassium iodide (the initial boundary of the AgI crystal is denoted by a dotted line).

The construction of a crystal lattice can be completed not only by ions of the lattice but also by ions isomorphous with them, and by atomic groups similar to those on the surface and forming a strong bond with the crystal surface. For example, coal firmly retains organic radicals, whereas oxides and hydroxides of aluminium and iron firmly bind groups containing oxygen.

Both ions and the molecules from which they are formed can be adsorbed on the adsorbent surface, and adsorption equilibrium exists between the former and the latter. V. Kargin has shown for ferri and alumino sols that a molecular form of an adsorbed electrolyte is present on the surface of colloidal particles.

3. EXCHANGE ADSORPTION

If an electrolyte is already adsorbed on the adsorbent surface, *exchange adsorption* or, to be more correct, ion exchange between the double electric layer of the adsorbent and the medium is observed

when the sorbent comes into contact with another electrolyte. In exchange adsorption, the adsorbent adsorbs a definite amount of some ions and at the same time discharges into a solution an equivalent amount of other ions of the same sign that were displaced from the surface.

Not only extraneous ions can exchange with the adsorbed adsorbents but also ions which are formed from the adsorbent upon dissociation of its molecules. In this case, the surface phenomenon of adsorption can become a volume phenomenon, i.e., ions buried in the deep layers of the adsorbent can participate in exchange if a solution can only get to them. In particular, this occurs in ion exchange on Permutite-Na^+ and other ion-exchange resins which we will deal with later. Of course, substances capable of undergoing volumetric ion exchange have a high capacity for adsorbing the appropriate ion from the solution.

Exchange adsorption has several distinguishing features.

First, exchange adsorption is specific, i.e., only definite ions are capable of undergoing exchange. In other words, exchange adsorption is strongly affected both by the nature of a solid phase with a double electric layer on it, and by the nature of the ion being adsorbed. Adsorbents may be acidic or basic, depending on the chemical nature of ions which can be exchanged with ions of adsorbents. Acidic adsorbents act as an acid and are capable of exchanging cations with solutions; basic adsorbents are similar to bases and they exchange anions. There are also many amphoteric adsorbents which exchange cations under some conditions, and anions under others. By its specific nature, exchange adsorption is similar to a chemical phenomenon.

Second, exchange adsorption is not always reversible.

Third, exchange adsorption occurs more slowly than molecular adsorption. It occurs particularly slowly in the course of exchange of ions which are buried deep in the adsorbent. Apparently, it takes time for ions to diffuse from the solution deep into the adsorbent and to displace ions which should pass over to the solution.

Fourth, the pH of the medium may change in this process, if a hydrogen or a hydroxyl ion is being exchanged by the adsorbent. If the adsorbent changes the hydrogen ion for a cation, the pH of the medium decreases and the adsorbent acts as an acid. If the adsorbent changes the hydroxyl ion for an anion, the pH of the solution increases and the adsorbent acts as a base. Ion exchange in both cases can be schematically illustrated as follows:

$$\text{adsorbent}^-\text{H}^+ + \text{Na}^+ + \text{Cl}^- \longrightarrow \text{adsorbent}^-\text{Na}^+ + \text{H}^+ + \text{Cl}^-$$

$$\text{adsorbent}^+\text{OH}^- + \text{Na}^+ + \text{Cl}^- \longrightarrow \text{adsorbent}^+\text{Cl}^- + \text{Na}^+ + \text{OH}^-$$

B. Nikolsky (1939) proposed an equation that qualitatively characterizes the exchange of ions *1* and *2* on a solid surface:

$$\frac{g_1^{1/z_1}}{g_2^{1/z_2}} = k\frac{a_1^{1/z_1}}{a_2^{1/z_2}} \tag{6.5}$$

where g_1, g_2 = content of ions being exchanged in the adsorbent, g-equiv/g;
a_1, a_2 = activities of ions being exchanged in the solution;
z_1, z_2 = valency of ions;
k = constant.

When $z_1 = z_2 = 1$, the equation is simplified to

$$g_1/g_2 = k'\,(a_1/a_2) \tag{6.6}$$

When electrolytic concentrations are small, the value of concentration c can be used instead of activity a. Then, Eq. (6.6) which connects the adsorbability of ions *1* and *2* with their concentration in a solution, becomes

$$g_1/g_2 = k'\,(c_1/c_2) \tag{6.7}$$

Exchange adsorption is important in agriculture, biology, and industry. The soil is capable of absorbing and retaining definite ions, such as the cations K^+ and NH_4^+ which are contained in fertilizers and are required by plants for their nutrition. In exchange for these cations, the soil discharges equivalent amounts of other cations, such as Ca^{2+} and Mg^{2+}. Cl^-, NO_3^-, SO_4^{2-}, and other anions are hardly adsorbed by the soil. According to K. Gedroits (1933) who thoroughly investigated ion exchange in the soil, the adsorbing complex, i.e., a highly dispersed mixture of insoluble aluminosilicates and organomineral compounds, is capable of adsorbing bases. Physical and agrotechnological properties of the soil depend to a considerable extent on the nature of adsorbed ions.

In industry, exchange adsorption is quite important. For example, when plant fibre is being dyed, it adsorbs coloured cations of the dye from the medium, discharging an equivalent amount of calcium ions which are always present in an industrial fibre. Exchange is very often caused not by the very substance of the adsorbent but by the minor impurities contained in the adsorbent.

Exchange adsorption is widely used in softening water. The presence of large amounts of hard salts (the ions Ca^{2+} and Mg^{2+}) in water often makes it difficult to use such water in industry. Soaps in hard water become insoluble calcium and magnesium soaps, losing their detergent and stabilizing action. When hard water is used in steam boilers, scales are formed on their walls; this reduces heat conduction, increases heat loss, and in some cases causes the boiler to explode (owing to local superheating and the gradual change in the metal

structure). Food boiled in hard water is usually tasteless and hard. To soften hard water, Gans proposed using an aluminosilicate adsorber which he called Permutite and whose composition can be expressed by the formula $Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$.

At present, natural minerals, glauconites, are also used instead of the relatively expensive Permutite-Na^+ to soften water.

The softening of hard water by Permutite can be explained by the scheme

$$\text{Permutite}^{2-}2Na^+ + Ca^{2+} + SO_4^{2-} \longrightarrow \text{Permutite}^{2-}Ca^{2+} + 2Na^+ + SO_4^{2-}$$

Permutite in which Na^+ was exchanged by Ca^{2+} can, according to the law of mass action, be readily regenerated again by treating it with a concentrated solution of NaCl. Then, Na^+ ions displace Ca^{2+} ions into the solution, and Permutite can be used again after it is washed. Thus, hard water is softened but not demineralized when it is treated with Permutite.

Ion-exchange resins are now widely used instead of Permutite and glauconite for softening water; they will be described in greater detail in Chap. 14.

Exchange adsorption is also used for trapping valuable substances from extremely diluted solutions, from which it is unprofitable to isolate these substances by other methods. Hence, it is possible to regenerate: copper from mine waters and from waste waters of the cuprammonium rayon industry; silver from the waste waters of factories manufacturing motion-picture films; chromium from electrolytic chromium baths, and so forth. Moreover, exchange adsorption is used to extract radioactive elements from solutions.

The exact establishment of the equivalence point when solutions are titrated in analytical chemistry is also based on exchange adsorption. For example, if a solution of sodium chloride is titrated with a solution of silver nitrate in the presence of fluorescein, an electric double layer consisting of Cl^- and Na^+ ions will originate on the surface of the AgCl crystals being formed as long as the solution contains even a small excess of sodium chloride. As a result, the precipitate being formed will be white and the solution will be yellow-green. However, a double layer of Ag^+ and NO_3^- ions will be formed on the surface of the AgCl crystals as soon as a small excess of silver nitrate appears in the solution. Since the coloured fluorescein anion possesses great adsorbability, it will displace the NO_3^- ion from the electric double layer and the precipitate will become yellow-green whereas the solution will become colourless. Such a colour change occurs very abruptly, and thus the equivalent point can be easily established in titration.

Exchange adsorption on coal. Coal which has no polarity should not adsorb ions of strong electrolytes. However, experiments show

that not only is coal capable of selectively adsorbing ions of electrolytes, but exchange adsorption can occur on it as well. Since coal is one of the most important adsorbents, let us consider the mechanism of exchange adsorption on it in detail.

Charcoal of plant or animal origin is capable of exchange adsorption owing to the presence of small amounts of inorganic substances in it. For example, coal adsorbs coloured cations of methylene blue from its solution and, in exchange, gives away colourless Ca^{2+} cations to the solution. However, coals which do not contain inorganic components are also capable of exchange adsorption. In this case, exchange adsorption can be explained by the purely electrochemical concepts evolved by A. Frumkin and by the concepts of surface compounds worked out by N. Shilov and his school.

According to Frumkin, coal can behave as a gas electrode which resembles a hydrogen electrode obtained by saturating platinum black with molecular hydrogen. The coal surface can adsorb hydrogen which is formed when coal is being produced and activated. Coal can also adsorb oxygen from the air when coal is being produced, activated, and stored. Coal can be either a hydrogen or an oxygen electrode, depending on what the coal surface is saturated with.

The hydrogen ion is formed on the surface of coal which has adsorbed molecular hydrogen when it comes into contact with water; the hydrogen atom is the donor, and coal is the acceptor of electrons:

$$\text{coal } H_2 \longrightarrow \text{coal}^{2-}\ 2H^+$$

Such coal in a solution of an electrolyte can exchange hydrogen ions for any other cations. For example, if a solution contains sodium chloride, the following exchange process will occur:

$$\text{coal}^-\ H^+ + Na^+ + Cl^- \longrightarrow \text{coal}^-\ Na^+ + H^+ + Cl^-$$

In this case, coal behaves as an acidic adsorbent, and the solution is acidified after exchange.

Coal on whose surface oxygen is adsorbed is an electron donor in water while oxygen atoms are electron acceptors:

$$\text{coal } O_2 \longrightarrow \text{coal}^{4+}\ 2O^{2-}$$

The very unstable O^{2-} ions immediately react with water, forming hydroxyl ions:

$$\text{coal}^{2+}\ O^{2-} + H_2O \longrightarrow \text{coal}^{2+}\ 2OH^-$$

In a solution of an electrolyte, such coal behaves as a basic adsorbent which exchanges hydroxyl ions for any anions:

$$\text{coal}^+\ OH^- + Na^+ + Cl^- \longrightarrow \text{coal}^+\ Cl^- + Na^+ + OH^-$$

The solution of the neutral electrolyte is alkalinized after exchange.

Frumkin's theory is supported by the fact that coal from whose surface adsorbed gases are removed by thorough evacuation loses the ability to adsorb electrolytic ions from the solution.

Shilov explained exchange adsorption on de-ashed coal from quite a different standpoint. According to him, very thin layers of oxides, which are not a new phase and are firmly bound to the crystal lattice of the adsorbent, are formed on the surface of coal when it is being produced or activated. These oxides can, while reacting with water, produce carboxyl groups that exchange hydrogen for a cation. In other words, such coal behaves as an acid. When coal is obtained under other conditions, hydroxyl groups may be formed on its surface when coal reacts with water. Such coal can exchange a hydroxyl for an anion, and thus it is a base. If coal is obtained or activated under intermediate conditions, when approximately the same number of carboxyl and hydroxyl groups is formed on its surface, it will have amphoteric properties, and the pH of the solution will not change.

Coal obtained by special purification or from pure substances (e.g., sugar) and containing no ash adsorbs acids from aqueous solutions, and remains indifferent to alkalis. Such coal adsorbs also anions from solutions of inorganic neutral salts (NaCl, KCl, KNO_3, K_2SO_4, and so forth). Since a certain number of $\equiv C—OH$ groups are always present on the coal surface, the hydroxyls of these groups enter the solution as OH^- ions in exchange for anions, i.e., exchange adsorption occurs, changing the pH of the system. Such adsorption is known as *hydrolytic adsorption.*

When Frumkin's and Shilov's theories of exchange adsorption on coal are considered in detail, it turns out that they do not contradict each other, but are interpretations of the same phenomenon from different standpoints, because Shilov's surface compounds in water are capable of being ionized and of forming an electric double layer of the gas electrode.

4. WETTING PHENOMENA

Wetting phenomena are similar to the adsorption phenomenon, and they are also determined by the intensity of interaction between molecules of different substances. Let us consider wetting phenomena by taking the example of a drop of liquid deposited on the surface of a solid although, of course, we can also deal with the wetting of a liquid by a liquid.

Wetting and the contact angle. If the molecules of a liquid interact with the molecules of a solid to a greater extent than among themselves, the liquid spreads on the surface, or, as we usually say, wets it. The liquid spreads until it covers the surface of a solid or the liquid layer becomes monomolecular. Such complete wetting is

observed, for example, when a drop of water is deposited on the surface of clean glass.

The liquid does not spread if its molecules interact with one another to a greater extent than with the molecules of a solid. Conversely, the liquid collects on the surface into a drop which would be almost spherical were it not for the action of gravity. A similar case is observed when a drop of mercury is deposited on any non-metallic surface.

Besides these two extreme cases, there may be intermediate cases of incomplete wetting when a drop forms with a solid surface an equilibrium angle, known as the *contact angle* or the *wetting angle*; this depends on the ratio of the intensities of molecular forces which act, on the one hand, between molecules of a liquid, and, on the other, between molecules of a liquid and of a solid.

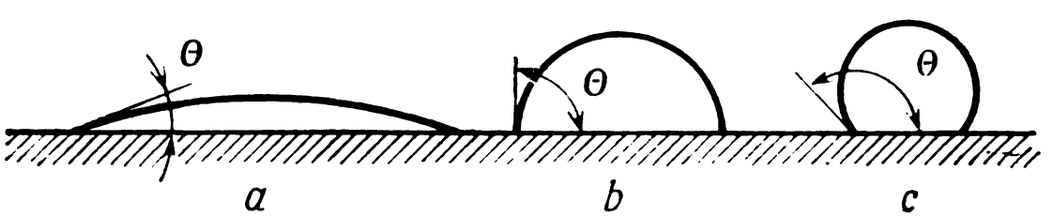

Fig. 6.7. Different cases of incomplete wetting:
a—$\theta < 90°$; *b*—$\theta = 90°$; *c*—$\theta > 90°$

Fig. 6.7 represents drops which, on a solid surface, form an acute contact angle ($\theta < 90°$), a right contact angle ($\theta = 90°$), and an obtuse contact angle ($\theta > 90°$). The contact angle formed by a drop on the surface of a solid is always measured from the liquid side. Complete non-wetting, i.e., when the contact angle is 180°, is hardly ever observed because forces of attraction, however small, always act between a liquid and a solid.

The values of contact angle formed by water on the surface of various solids in an air atmosphere are given below.

Quartz	Malachite	Galenite	Graphite	Talc	Sulphur	Paraffin
0°	17°	47°	55-60°	69°	78°	106°

A solid is wetted by a liquid as a result of the action of forces of surface tension. Let us consider the example of incomplete wetting illustrated in Fig. 6.8. Apparently, the wetting perimeter or circumference of a drop is the boundary of interaction of three media: liquid *1*, air *2*, and solid *3*. These media have interfaces: the liquid—air interface with a surface tension of $\sigma_{1,2}$, the air—solid interface with a surface tension of $\sigma_{2,3}$, and the liquid—solid interface with a surface tension of $\sigma_{1,3}$. Hence, three forces, $\sigma_{1,2}$, $\sigma_{2,3}$ and $\sigma_{1,3}$, act per unit length of the wetting perimeter. Here, these forces are denoted by vectors; they are perpendicular to elements of the circumference and tangential to the respective interface. For the equili-

brium contact angle θ to be formed, all the three forces must counterbalance one another. Forces $\sigma_{2,3}$ and $\sigma_{1,3}$ act in the plane of the solid surface while force $\sigma_{1,2}$ is directed to the surface at an angle of θ. However, since the point of application of the three forces can move

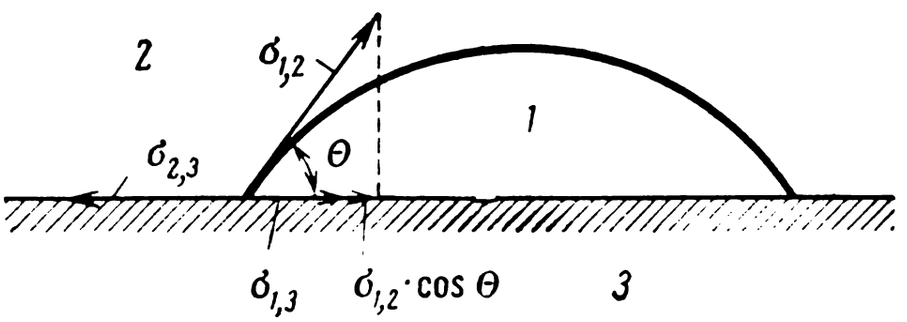

Fig. 6.8. Relationship between the contact angle and surface tensions $\sigma_{1,2}$, $\sigma_{2,3}$ and $\sigma_{1,3}$:
1—liquid; *2*—air; *3*—solid

only on the surface but cannot tear away from it, instead of force $\sigma_{1,2}$, it is necessary to take its plane projection, i.e., $\sigma_{1,2} \cos \theta$. The condition of equilibrium of forces is then expressed by Young's equation

$$\sigma_{2,3} = \sigma_{1,3} + \sigma_{1,2} \cos \theta \tag{6.8}$$

After solving this equation in respect to cos θ, we obtain

$$\cos \theta = \frac{\sigma_{2,3} - \sigma_{1,3}}{\sigma_{1,2}} \tag{6.9}$$

Besides the "force" derivation given above, Young's equation can be also derived thermodynamically. Here is this derivation according to Adamson.

Let us imagine that a liquid has moved along the surface by a very small distance and covered the surface area of a solid equal to Δs. Taking into account that specific interfacial energies are numerically equal to the respective values of surface tension, a change in the free surface energy ΔF is equal to

$$\Delta F = \Delta s (\sigma_{1,3} - \sigma_{2,3}) + \Delta s \sigma_{1,2} \cos (\theta - \Delta\theta)$$

or

$$\Delta F / \Delta s = \sigma_{1,3} - \sigma_{2,3} + \sigma_{1,2} \cos (\theta - \Delta\theta)$$

In equilibrium, $\lim_{\Delta s \to 0} \Delta F / \Delta s = 0$

Then

$$\sigma_{1,3} - \sigma_{2,3} + \sigma_{1,2} \cos \theta = 0$$

Whence we obtain

$$\sigma_{2,3} = \sigma_{1,3} + \sigma_{1,2} \cos \theta$$

$$\cos \theta = \frac{\sigma_{2,3} - \sigma_{1,3}}{\sigma_{1,2}}$$

The quantity cos θ which characterizes the ability of a liquid to wet the surface is known as *wetting* and denoted by B. Apparently, in complete wetting ($\theta = 0$), $B = +1$ and in the hypothetical case of complete non-wetting ($\theta = 180°$), $B = -1$. Since a liquid wets a solid better when there is less interaction between its molecules, non-polar liquids having small surface tension wet the surface well. For example, hydrocarbons having a surface tension of 20-30 erg/cm^2 wet almost all solids; water having a surface tension of 72.75 erg/cm^2 (at 20°C) wets only some bodies, such as glass, quartz, and inorganic salts; mercury having a surface tension of 475 erg/cm^2 wets only some metals.

Wetting is a process in which free energy decreases in a system consisting of three contacting phases. Indeed, suppose that a very thin layer of liquid *1* spreads on the surface of solid *3* which is in medium *2*, and suppose that the area covered by the liquid thus increases by Δs. In this case,

(1) the surface of solid *3* which is in contact with medium *2* decreases by Δs, as a result of which the surface energy of the system decreases by $\sigma_{2,3}\,\Delta s$;

(2) the surface with which liquid *1* contacts medium *2* increases by Δs, as a result of which surface energy grows by $\sigma_{1,2}\Delta s$;

(3) the interfacial area of liquid *1* and solid *3* grows by Δs, as a result of which the surface energy of the system increases by $\sigma_{1,3}\Delta s$.

Hence, the total change in free surface energy F when the liquid spreads is

$$\Delta F = (-\sigma_{2,3} + \sigma_{1,2} + \sigma_{1,3})\,\Delta s$$

whence

$$\Delta F/\Delta s = \sigma_{1,3} + \sigma_{1,2} - \sigma_{2,3} \tag{6.10}$$

But it follows from Eq. (6.8) that when the liquid spreads and completely wets the surface ($\cos\theta = 1$), the condition given below must be met:

$$\sigma_{2,3} > \sigma_{1,3} + \sigma_{1,2}$$

or

$$\sigma_{1,3} + \sigma_{1,2} - \sigma_{2,3} < 0 \tag{6.11}$$

By comparing Eqs. (6.10) and (6.11), we may conclude that the liquid spreads and wets the surface if the energy of the system decreases.

Proceeding from the general condition of minimum surface energy when the contacting media are in equilibrium, the loss of free surface energy as the liquid—solid interface is formed can be taken as a measure of wetting a body by a liquid. It follows that a given surface is wetted better by a liquid whose spread causes a decrease in the surface energy of a system by a greater quantity than that in

the case of another liquid. Since wetting is accompanied by a decrease in surface energy, heat is liberated in the wetting process. The heat of wetting per square centimetre of a surface usually ranges from 10^{-3} to 10^{-5} cal. The heat of wetting (i.e., heat of immersion) can serve as a characteristic of the ability of a liquid to wet the surface of a solid if the contact angle of wetting cannot be determined, for example, when powders are wetted by a liquid.

The wetting phenomenon can be observed also when, instead of air, another liquid is taken that does not mix with the first one and has lower density. If each of the two liquids can wet the surface, there will apparently be competition between them that is similar to competition in the adsorption of two adsorptives. Wetting is determined by the ratio of molecular forces acting between molecules of each liquid, on the one hand, and between molecules of liquids and molecules of a solid, on the other; therefore, it is not difficult to see that, between the two liquids, the liquid whose value of polarity is closer to that of a solid will wet the surface. The liquid which wets the surface better is said to have great selective wetting in respect to the given surface.

Selective wetting was investigated by P. Rehbinder. Let us consider this phenomenon in greater detail. Suppose that the surface of a solid is in contact with polar water and some non-polar hydrocarbon. Then, the surface is said to be *hydrophilic* if water selectively wets the surface, i.e., if the contact angle θ formed from the side of water is less than 90° and the value of $B = \cos\theta > 0$. According to Eq. (6.9), this occurs when $\sigma_{2,3} > \sigma_{1,3}$ or when $\sigma_{2,3} - \sigma_{1,3} > 0$. Selective wetting by water is usually observed when the difference in the polarities between water and a solid is less than that between a non-polar hydrocarbon and a solid. Substances with a hydrophilic surface are characterized by strongly pronounced intermolecular interaction; these are quartz, glass, corundum, gypsum, and malachite, i.e., silicates, carbonates, sulphates, and oxides and hydroxides of metals. Cellulose is among the organic substances having a hydrophilic surface.

A surface is said to be *hydrophobic* or *oleophilic* if a solid is wetted better by a non-polar hydrocarbon, i.e., if $\theta > 90°$ for water, and the value of $B = \cos\theta < 0$. According to Eq. (6.9), this can be observed only when $\sigma_{2,3} < \sigma_{1,3}$ or when $\sigma_{2,3} - \sigma_{1,3} < 0$. Selective wetting by a non-polar hydrocarbon is observed when the difference in polarities between a hydrocarbon and a solid is less than that between water and a solid. Substances having a hydrophobic surface are all the hydrocarbons and other organic compounds with large hydrocarbon radicals, and inorganic compounds such as sulphides of heavy metals, talc, graphite, and sulphur.

When the contact angle is 90°, an intermediate case will be observed, selective wetting being absent.

If all the minerals are arranged in a series according to the growth of their hardness, the series, as Rehbinder has indicated, coincides with the series of the same minerals arranged according to their selective wettability by water. Minerals of high hardness, i.e., quartz, corundum, and diamond, are very hydrophilic.

In many textbooks and monographs, the terms "hydrophilic" or "hydrophobic" surface are applied to the surface on which water forms an acute or an obtuse contact angle, respectively, at the boundary with air. This is the wrong way of determining the hydrophilic or hydrophobic nature because most surfaces produce acute contact angles with water in an air atmosphere. But a different picture is observed when a surface is selectively wetted by water in the presence of a non-polar liquid. In this case, water by no means forms always an acute contact angle. Under these conditions, hydrophilic surfaces are selectively wetted by water, and the contact angles $\theta < 90°$; however, if the surfaces are hydrophobic, hydrocarbon partially displaces water, and for water $\theta > 90°$.

Determination of the contact angle. To measure the contact angle formed by a liquid on a solid, a small drop of liquid is deposited on the surface of a solid, and a side image of the drop is projected on a screen by means of a beam of light directed parallel to the surface; then, the contour of the drop is traced on the screen, and a tangent to the contour of the drop is drawn through the point where all the three phases come into contact. The inclination angle of this tangent is the contact angle.

To measure the contact angle formed by two immiscible liquids on the surface of a solid substance, a plate made of this substance is immersed in a glass cuvette containing a lighter liquid, and then a drop of a heavier liquid is carefully deposited on the plate surface by a pipette. Everything else is the same as in the preceding case.

Besides this extremely simple, but not very precise, method of determining the contact angle, there are other, more precise, but at the same time more complicated, methods which are considered in courses in practical colloid chemistry.

It is often difficult to determine the true value of the contact angle for the reasons given below.

1. The contact angle may be affected by traces of substances which contaminate the surface. Wetting sharply changes when a contaminant forms a monomolecular layer on the surface, and this requires negligible quantities of it. According to some authors, surface wetting can be affected even when a surface comes into contact for some time with the air of industrial towns which always contains traces of hydrocarbons.

2. Many substances, such as metals, are oxidized well and a very thin, hardly detectable oxide film is formed on their surface. This

film can also greatly affect wetting. Therefore, surfaces taken for determining the contact angle should not be contaminated or oxidized.

3. Surfaces usually adsorb air well. Naturally, the adsorbed air retards the spread of a liquid along a solid because a certain length of time is required for displacing air from the surface and establishing an equilibrium contact angle. Such a retardation of the establishment of the equilibrium contact angle is known as *wetting hysteresis.* In many cases, the equilibrium contact angle may not be established at all because of hysteresis.

Hysteresis is expressed in the fact that the contact angle very often depends on the conditions under which it is formed. For example, if a drop of a liquid is pressed against the surface of a solid, the contact angle will be smaller than when the drop is carefully deposited on the surface. In capillaries whose walls are wetted incompletely, the liquid rises to a different height because of hysteresis, depending on whether it rises freely along the capillary, or whether the capillary is filled and then the liquid is allowed to run off until an equilibrium position is attained.

Hysteresis also causes the contact angle formed when a liquid flows up to be larger than when it flows down. The latter phenomenon can be observed when raindrops run down a window pane which is not too clean: the drops are held back, as it were, and form a much larger contact angle at the bottom than on the top.

To eliminate hysteresis that is caused by air adsorption, the method of determining the contact angle may be modified in the following way. A plate of a solid substance is placed into a glass cuvette containing a liquid, and after its surface is completely wetted, it is put horizontally. A bubble of air is then introduced under the plate, without taking it out of the liquid, with a pipette whose tip is bent. The contact angle is then determined from the liquid side in the same way as described above.

4. The roughness of a surface of a solid can affect its wetting; the greater the roughness, the more clearly are the surface properties causing the attraction or repulsion of water exhibited. Such an effect can be explained by the fact that at $\theta < 90°$ (for a smooth surface), the liquid penetrates into the cavities of the surface in a similar way as it is imbibed by the capillaries it wets. Of course, this improves the wetting of a rough surface. If $\theta > 90°$, the liquid does not penetrate into the cavities and this worsens the wetting of a rough surface. In other words, roughness makes a hydrophilic surface more hydrophilic, and the roughness of a hydrophobic surface makes it still more hydrophobic. To prevent the effect of the microrelief, the surface of the test solid must be as smooth as possible.

Wenzel was the first to indicate how to take into account the effect of the roughness of a surface on its wetting by a liquid. Surface

tensions $\sigma_{2,3}$ and $\sigma_{1,3}$ which are in the calculating equation (Young's equation) should accordingly be multiplied by the roughness factor r, i.e., the ratio of the actual interface area to the surface area of a solid if it were smooth.* As a result, instead of Young's equation, we may write

$$r(\sigma_{2,3} - \sigma_{1,3}) = \sigma_{1,2} \cos \theta$$

5. The contact angle can be affected by the conditions under which a surface is formed. For example, the surface of stearic acid, obtained by cooling its melt in air, is hydrophobic. But the surface of stearic acid, obtained by cooling its melt on the boundary with glass, turns out to be hydrophilic. This phenomenon can be explained by the fact that, in the former case, mainly the hydrophobic hydrocarbon radicals of stearic acid face air whereas in the latter case, the polar hydrophilic carboxyls are turned outwards owing to the action of the polar glass surface on the melt.

In general, we may speak of the *surface* and *volume hydrophily* (or *hydrophobicity*) of a substance because of the definite orientation of its molecules in the surface layer. V. Pchelin has shown that the surface of an animal hair is hydrophobic whereas the very substance of the hair is hydrophilic.

In practice, the most important case is when the wetting liquid is water. Non-polar substances, e.g., surfaces covered with hydrocarbons, are poorly wetted by water. To improve wetting by water, we usually use wetting agents, i.e., soluble, well adsorbing substances and surfactants which reduce surface tension at the solid—liquid interface and, at the same time, at the liquid—air interface. When a wetting agent is deposited on a surface, the contact angle, being a measure of wetting, diminishes as a result of a decrease in the values of $\sigma_{1,3}$ and $\sigma_{1,2}$ in conformity with Eq. (6.9), and wetting accordingly grows.

Molecules of a wetting agent are usually diphilic, as is characteristic of any surfactant, and they are adsorbed on the water surface, with their hydrocarbon chains being oriented outwards into the air, so that a hydrocarbon film is formed, as it were, on the water surface. This explains the decrease in the surface tension of a solution (and an increase in wettability) to values typical of organic non-polar liquids.

Monolayers of surfactants can pass over from a solution to a solid surface and form a polymolecular layer on it. This property was discovered long ago by Blodgett in the following experiment. A glass plate is carefully introduced in a vertical position into a monomole-

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* For greater details on hysteresis, see S. S. Voyutsky, *Fiziko-khimicheskie osnovy propityvaniya i impregnirovaniya voloknistykh materialov dispersiyami polimerov* (Physico-chemical Principles of Impregnating Fibrous Materials with Polymer Dispersions). Khimiya, Leningrad, 1969, p. 13.

cular, closely packed layer of surfactant molecules which is formed on the water surface. When this plate is being immersed, its hydrophilic surface is covered with a monomolecular surfactant layer; the polar part of the surfactant molecules is turned to the polar surface of glass, and the plate surface thus becomes hydrophobic. Afterwards, the plate together with the layer of the surfactant adsorbed on it is carefully taken out of the solution. The plate has already adsorbed a monomolecular layer of a surfactant; now it adsorbs another layer of the same substance, with the non-polar radicals of molecules in this layer facing the non-polar radicals of the first layer, i.e., being turned towards the plate. As a result, a bimolecular layer of molecules, with their non-polar radicals facing one another, is formed on the plate surface which becomes hydrophilic again. A number of layers of a surfactant can be transferred to the plate by repeating this operation many times, making the plate surface hydrophobic and hydrophilic by turns.

Practical importance of wetting. Wetting is important for successful effecting several technological processes. For example, in the textile technological process, the good wetting of fibre or textiles is a prerequisite of dyeing, bleaching, desizing, impregnating, laundering, and so forth. Wetting is significant in the effective use of insecticide-fungicide combinations because the leaves of plants and the wool of animals are always hydrophobic. Wetting is also important in printing. The mechanical treatment (cutting, drilling, polishing) of metals and non-metallic bodies is accelerated and facilitated when they are wetted by the appropriate liquids. It is also easier to bore oil wells in rocks when special boring solutions which contain wetting agents are used. In tinning, soldering, and welding metals, and also in pasting together various solids, it is necessary to wet their surfaces well. Selective wetting is the basis of ore concentration, i.e., flotation. Let us consider, as an example, the role of wetting in such processes as laundering, impregnation, and flotation.

The purpose of laundering is to remove impurities, such as the yolk of wool, size, soot, dust, and proteins, from the surface of a solid which is usually a fibre or a textile. In laundering, the fibre—impurity interface is replaced by the interfaces between the fibre and the detergent solution, and between the impurity and the detergent solution. The processes on which laundering is based differ from selective wetting only by the fact that a solid impurity or a semi-solid impurity acts as the first liquid.

Let us consider the laundering process by taking the example of the removal of a liquid hydrocarbon (fat) from the surface of a textile by means of ordinary soap. The engineer's job is to reduce as much as possible surface tension at the interfaces between the detergent solution and the impurity, and between the detergent solution

and the fibre. Tensions of these surfaces decrease after the adsorption of soap on the surfaces of fat and textile; of course, adsorption occurs in a way that the polar parts of soap molecules are turned towards water, and their non-polar parts, towards an impurity or a fibre. Fat then collects into a drop under the action of unchanged surface tension at the solid—impurity interface, and the drop may be easily

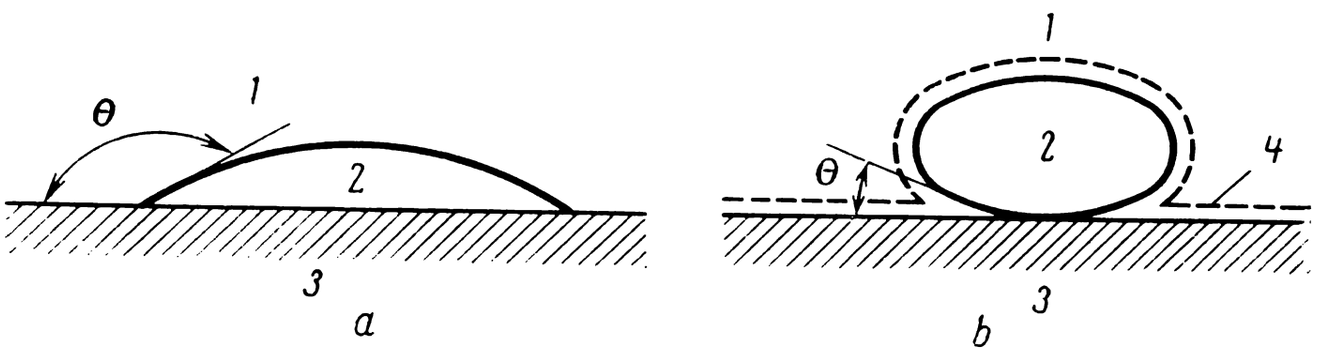

Fig. 6.9. Diagram of the washing of a hydrocarbon in laundering by a liquid which wets the surface (*a*) and by a liquid which does not wet the surface (*b*): *1*—soapy solution; *2*—hydrocarbon; *3*—textile; *4*—hydrophilic detergent layer

removed from the fibre surface by even inconsiderable mechanical action. Washing occurs, consisting in a sharp growth of $B = \cos\theta$ (for water), i.e., in a diminution of the contact angle. This is shown in Fig. 6.9.

In laundering, detergent *1*, while being adsorbed both on the surface of textile *3* and on the surface of a hydrocarbon particle *2* contaminating the textile, forms a hydrophilic soap layer *4* on them. This layer helps to separate the particles of an impurity from the textile because, if the surface being washed is better wetted by water under the conditions of selective wetting, it is worse wetted by a hydrocarbon. Moreover, the layer of hydrated, partially ionized soap molecules that is formed on the hydrocarbon drops makes the emulsion which has originated stable and thus helps to remove the impurity together with the detergent solution at the end of laundering.

The adsorbing soap molecules can orient their polar groups towards the fibre, and their non-polar hydrocarbon radicals, into the detergent solution, on the surface of a bleached hydrophilic textile owing to the polarity of cellulose. It would seem that the surface should become hydrophobic in this case, reducing the laundering effect. However, when sufficiently concentrated soap solutions are used, after the first molecular layer has originated, the second soap layer whose molecules are oriented in the opposite direction, i.e., their polar groups are in the detergent solution, is formed on the textile surface which becomes hydrophilic.

Rehbinder believes that sufficient mechanical strength and viscosity of hydrated adsorption layers of a detergent are also a prerequisite for detergency. On the one hand, such layers at the interface

between the detergent solution and air promote foaming which is important in laundering. On the other, when stable hydrated adsorption layers are formed around particles of fat, impurities washed off are emulsified and will not settle again on the fibre.

A process which is to a certain extent the opposite of laundering, is the impregnation of textiles; it is intended to increase their water-impermeability while preserving their air-permeability (what is called *porous water-repelling impregnation*). The engineer's job is to form thin films on the surface of textile fibrils, so that water will form a large contact angle on the films. Textiles are accordingly impregnated with solutions or dispersions of such hydrophobic, or water-repelling, substances as aluminium acetate, soaps of polyvalent metals, paraffin, asphalt, oil residues, organosilicon compounds, and mixtures of these substances. Sometimes, textiles are impregnated in two procedures in order to increase their water-impermeability. For example, a textile is impregnated at first with a dispersion of paraffin which contains soap as an emulsifier, and then with an aluminium acetate solution; in this case, paraffin particles are deposited on the fibre as a result of coagulation.

After impregnation, the textile is dried, and films of water-repelling substances are formed on its fibrils. When a textile is impregnated with a dispersion, particles of a water-repelling substance are deposited discretely on the fibril surface. However, a hydrophobic substance usually melts and spreads along the fibre during subsequent drying at elevated temperature.

As a result of impregnation, the surface of textile capillaries becomes hydrophobic, non-wettable by water. Water is prevented from moving along such a capillary by great surface tension at the interface between water and the hydrophobicized surface; this tension reduces the surface of contact between water and the capillary walls, and does not allow water to run along the walls. Therefore, water, while penetrating into the opening of the capillary, does not wet its walls, but forms a convex meniscus, as is shown in Fig. 6.10. The curved surface of this meniscus tends to shrink and become level under the action of surface tension; then upward pressure begins which counterbalances the pressure of water trying to penetrate into the capillary. Of course, the higher the surface tension and the narrower the capillary, the greater is the pressure which can force water through the capillary. Consequently, in order to obtain a textile having high water-impermeability, the textile being hydrophobicized must be sufficiently thick and contain no surfactants (residues of emulsifiers of an emulsion with which impregnation was effected).*

* For greater details on the mechanism of impregnation, see S. S. Voyutsky, *Fiziko-khimicheskie osnovy propityvaniya i impregnirovaniya voloknistykh materialov dispersiyami polimerov* (Physico-chemical Principles of Impregnating Fibrous Materials with Polymer Dispersions). Khimiya, Leningrad, 1969, p. 236.

The phenomena of wetting and non-wetting are also the basis of the flotation process, i.e., a method of concentrating minerals which is now widely used. This method is based on different wetting of particles, which are being separated, by water. To make it clear, let us consider the behaviour of sufficiently small hydrophobic and hydrophilic mineral particles at the water—air and water—oil interfaces.

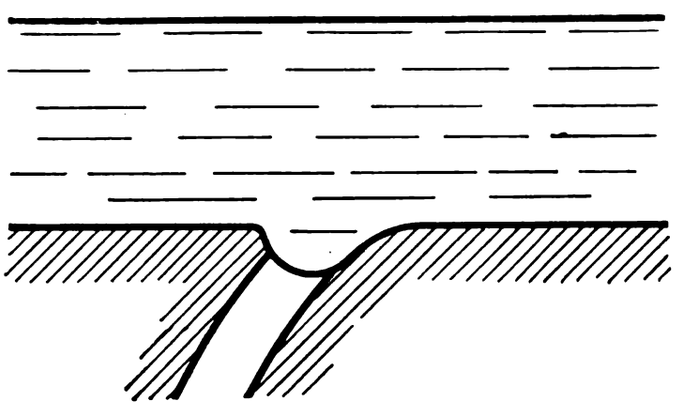

Fig. 6.10. Non-wetting of the capillary of a hydrophobicized textile by water

Hydrophilic particles are wetted by water and are drawn into it under the action of surface tension at the water—air or water—oil interface. Besides the force of surface tension, gravity also acts on the particle. As a result, the particle passes into the aqueous phase and sinks.

Water does not wet hydrophobic particles, and the particle may remain at the interface under the action of surface tension at the

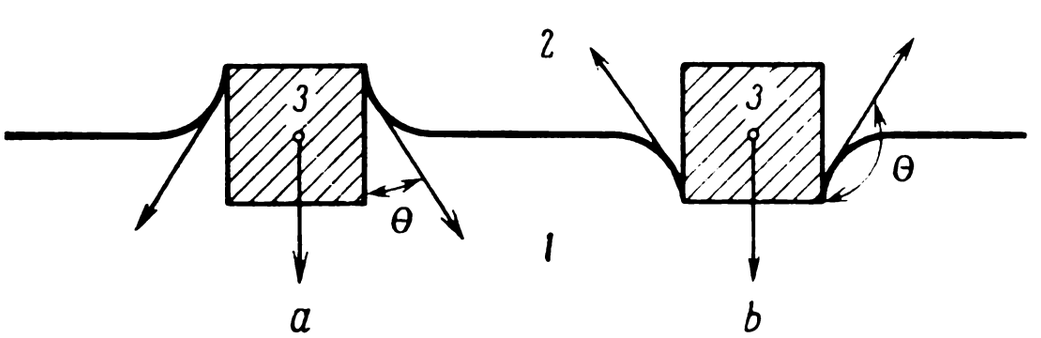

Fig. 6.11. Separation of hydrophilic (*a*) and hydrophobic (*b*) particles by flotation:
1—water; *2*—air or oil; *3*—solid

water—air or water—oil interface, provided the particle is not too large and gravity is not greater than the flotation force. Both of these cases are schematically illustrated in Fig. 6.11. Of course, when a mineral is ground to the required extent of dispersion, the size of particles at which they will remain on the surface can always be selected because, in crushing, gravity decreases in direct proportion to the cube of the radius of the particle whereas the flotation force decreases in direct proportion to the radius. However, an excessively

great degree of dispersion may be harmful since small particles are subjected to intensive Brownian motion, and this reduces the probability of their attachment at the water—air or water—oil interface.

The flotation concentration of mineral ores is based on the fact that sulphur compounds of metals in the ore are more hydrophobic than barren rock, such as quartz. The separation of ore by flotation is almost never effected by simply introducing ground ore into water whose surface borders on air or oil. In such form, the flotation process is too ineffective. At present, froth flotation is widely used. It consists in the introduction of air bubbles into the mineral suspension, i.e., the flotation pulp. When bubbles rise upwards, they accumulate on their surface the ore particles on which water forms a large contact angle. As a result, mineralized froth is collected on the pulp surface. The froth is removed from the pulp surface as an ore concentrate by means of gravity or with special rakers. Particles of barren rock that are well wettable by water do not adhere to the bubbles, but settle to the bottom and form flotation wastes, or "tailings".

The optimum size of mineral grains in flotation is 0.15-0.01 mm. However, mineral particles may be larger (0.5-1.0 mm) in the flotation of pit coal and native sulphur. The weight ratio of ore to water in the pulp is usually in the range of 1 : 4 to 1 : 2.

Let us consider the thermodynamics of froth flotation in the most general form. Let us accordingly calculate the change in the free energy of a system in froth flotation. Before flotation, the following equation can be written for the free interfacial energy F_0 of a system:

$$F_0 = \sigma_{1,2} s_{1,2} + \sigma_{1,3} s_{1,3} \tag{6.12}$$

where $\sigma_{1,2}$ and $\sigma_{1,3}$ = specific surface energy (which is numerically equal to interfacial tension) at the interfaces between the aqueous medium and air, and the aqueous medium and the substance being floated, respectively;

$s_{1,2}$ and $s_{1,3}$ = respective interfacial areas.

As a result of flotation, free energy of surface area s of contact between the particle being floated and air is

$$F_1 = \sigma_{1,2} (s_{1,2} - s) + \sigma_{1,3} (s_{1,3} - s) + \sigma_{2,3} s \tag{6.13}$$

Hence, the change in free energy as a result of flotation will be

$$-\Delta F = F_0 - F_1 = (\sigma_{1,2} + \sigma_{1,3} - \sigma_{2,3}) s \tag{6.14}$$

According to Eq. (6.8),

$$\sigma_{1,3} - \sigma_{2,3} = -\sigma_{1,2} \cos \theta \tag{6.15}$$

Substituting this equation in Eq. (6.14), we obtain

$$-\Delta F = (\sigma_{1,2} - \sigma_{1,2} \cos \theta) s = \sigma_{1,2} (1 - \cos \theta) s = \sigma_{1,2} (1 - B) s \tag{6.16}$$

The probability of flotation W is connected with a change in free energy by the equation

$$W \sim \exp(-\Delta F/RT) = \exp[\sigma_{1,2}(1-B)s/RT] \qquad (6.17)$$

Consequently, the probability of particle flotation grows with the surface tension at the water—air interface and with a decrease in the wetting of the particles being floated by the aqueous phase.

The difference between the hydrophobic nature of the surface of particles of a mineral and that of barren rock is usually small. Therefore, in order to make flotation more effective, *collectors* are almost always used. Collectors may be organic substances having diphilic molecules which are capable of being adsorbed on the surface of mineral particles in such a way that the polar parts of the molecules face the adsorbent, and the hydrocarbon radical is turned outwards. As a result, the particles of a mineral become more hydrophobic and the rate of flotation rises. Xanthates $RO-C\begin{matrix}S\\ \diagdown\\ SM\end{matrix}$ (where R is the hydrocarbon radical, and M is an alkali metal) are used most commonly as collectors. Presumably, xanthates are not simply adsorbed by the surface of particles of metal sulphides, but also react with them.

When non-sulphide minerals are being floated, fatty acids and their soaps are usually used as collectors. The ionogenic groups of these collectors are always turned to the solid, and therefore they are known as *solidophilic* groups. Such collectors are especially suitable for salt-like minerals having in their composition cations of alkaline-earth metals: Ca^{2+}, Mg^{2+}, Sr^{2+}. Ionic bonds prevail in the crystal lattices of these minerals, and their cations actively interact with the chemically adsorbed surface-active ions $RCOO^-$ of acids or soaps. The binding of collectors to the surface of the particles being floated is affected also by the length of the hydrocarbon chains whose interaction promotes the formation of the adsorption film, and the greater is such interaction, the more firmly are the adsorption layers of the collector bound to the surface of a mineral.

Non-polar minerals containing no metals and poorly wetted by water (graphite, sulphur, talc, coal) require less powerful, slightly water-soluble collectors, such as oils, at a comparatively low concentration: only several hundred grams of a collector is taken per ton of ore. Therefore, a very thin monomolecular, sometimes even an unsaturated, layer on the surface of mineral particles is enough to improve flotation.

Besides collectors, frothers and regulators are used in flotation.

Frothers are needed for obtaining a sufficiently (but not excessively) stable mineralized froth. They should not noticeably change the

wetting of the particles being floated, but should be adsorbed at the interface between the air bubble and the aqueous phase. Aliphatic alcohols can be used as frothers promoting flotation because their —OH group is weakly bound to the surface of mineral particles, but well adsorbed at the interface between the solution and the gas owing to the surface activity of alcohol.

In selecting frothers, substances which greatly reduce surface tension should not be taken; otherwise, froth will be barren, i.e., it will either not contain a mineral or contain it in a very small amount.

Regulators are used for controlling the selective action of collectors. In some cases, a regulator acts directly on the surface of a mineral, facilitates the interaction between it and the collector, and thus improves flotation. Such a regulator is an activator of flotation. In other cases, a regulator hinders the interaction between a mineral and the collector and this suppresses the flotation of the mineral. Such a regulator can be called a depressant. An example of an activator of flotation is sodium sulphide which improves the flotation of metal sulphides by means of xanthates. Liquid glass which worsens the flotation of silicate minerals can be used as a depressant.

Flotation can be used not only for isolating a product from a mineral, but also for separating several products. Such flotation is known as *selective flotation*, and it is effected with the aid of regulators. An example of this flotation is the flotation of lead and zinc ores when a lead concentrate is first obtained by introducing depressants into the pulp to prevent the flotation of zinc minerals; then, the floatability of zinc minerals is improved by activators, and they are transferred into froth, thus yielding a zinc concentrate.

Flotation is used on an ever wider scale for concentrating various minerals, such as sulphide ores, several ores of non-ferrous metals, e.g., lead-zinc, copper, copper-zinc, molybdenum, iron, tin and rare-metal ores, sulphur, graphite, coal, ores containing apatite, fluorspar, barite, and so forth. Flotation is also important because ores which are thinly intercalated in rock and whose resources are inexhaustible can be used.

5. ADHESION

Phenomena which resemble adsorption and wetting are the *adhesion* phenomena when either two mutually insoluble liquids, or a liquid and a solid, or two solids, are brought into close contact with each other; then, under the action of intermolecular or other (e.g., electric) forces, they strongly adhere to one another in such a way that a certain effort must be made or work must be done in order to separate them.

There are three cases of adhesion.

1. Adhesion between two liquids. Let us imagine that there are two liquids *1* and *3* in medium *2*, which are in contact with each other

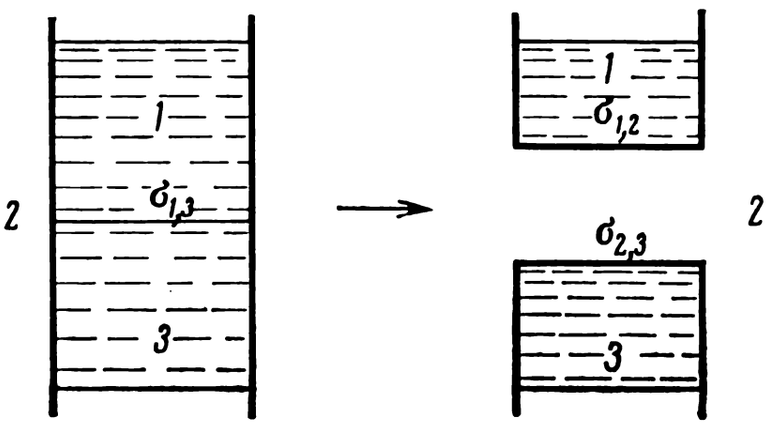

Fig. 6.12. Diagram showing the change in interfaces when immiscible liquids *1* and *3* are being separated in medium *2*

on area s, as is shown in Fig. 6.12. Two surfaces are then formed: that of liquid *1* having a surface tension of $\sigma_{1,2}$ and that of liquid *3* having a surface tension of $\sigma_{2,3}$, while the interface having a surface tension of $\sigma_{1,3}$ disappears. Hence, the work of adhesion, i.e., work required for separating the unit surface area of one liquid from another is

$$A/s = \sigma_{1,2} + \sigma_{2,3} - \sigma_{1,3} \qquad (6.18)$$

This equation was given for the first time by Dupré.

2. Adhesion between a liquid and a solid. Suppose that a drop of liquid *1* is on the surface of a solid *3* in medium *2*. The work of adhesion cannot be calculated by Eq. (6.18) in this case because the surface tensions $\sigma_{1,3}$ and $\sigma_{2,3}$ are usually unknown. However, $\sigma_{1,3}$ and $\sigma_{2,3}$ can be eliminated from Eq. (6.18) using Eq. (6.8). Then, the work of adhesion is

$$A/s = \sigma_{1,2} + \sigma_{1,2}\cos\theta = \sigma_{1,2}(1 + \cos\theta) \qquad (6.19)$$

3. Adhesion between solids. The work of adhesion cannot be determined here from the values of surface tension, because these values at the solid—air interface are usually unknown. B. Deryagin and N. Krotova have shown that the work of adhesion in this case is many times greater than work calculated on the basis of indirect theoretical assumptions, and that it depends on the rate of destruction of the adhesion contact. This indicates the non-equilibrium nature of the destruction of the adhesion contact between solids. To explain the adhesion of a solid to a solid, several theories have been proposed: the molecular theory which is often called, though not quite correctly, the adsorption theory (de Bruyn, McLaurin, and other authors); the electric theory which later evolved into the electron theory (Deryagin, Krotova, Smilga); the diffusion theory which is applicable to a particular case, i.e., the adhesion of a polymer to a polymer (Voyutsky), and so forth. It is most likely that there is no universal theory of adhesion of a solid to a solid. This phenomenon can be explained by different theories, depending on the nature of solids and the conditions under which an adhesion contact was formed.

7

ELECTRICAL PROPERTIES OF COLLOIDAL SYSTEMS

This chapter treats the electrical properties of highly dispersed colloidal systems having a solid dispersed phase and a liquid dispersion medium. The electrical properties of aerosols, emulsions, and solutions of colloidal surfactants will be dealt with in other chapters.

1. CONCEPT OF ELECTROKINETIC PHENOMENA

The fact that particles of disperse systems carry an electric charge was discovered by F. Reuss of Moscow University as early as 1808. He applied the electric potential gradient to electrodes which were immersed into glass tubes filled with water; the tubes were stuck

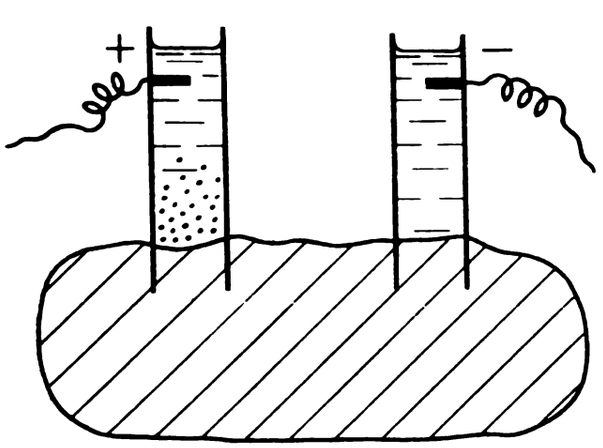

Fig. 7.1. Schematic illustration of the Reuss experiment in electrophoresis

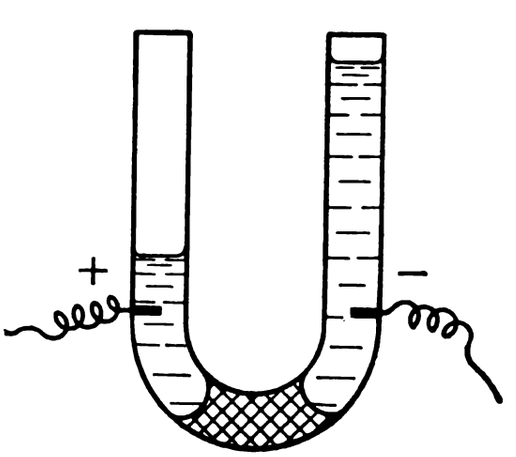

Fig. 7.2. Schematic illustration of the Reuss experiment in electroosmosis

into a piece of raw clay (see Fig. 7.1). The liquid in the tube with a positive pole grew cloudy while the water in the tube with a negative pole remained clear, indicating that clay particles in the electric field were transferred to the positive pole. As was discovered later, particles are transferred at a constant rate in the electric

field. This rate is the greater, the higher are the potential gradient applied and the dielectric constant of the medium, and it is the smaller, the greater is the viscosity of the medium. The transfer of particles in the electric field has become known as *electrophoresis* or *cataphoresis.*

In other experiments, Reuss put fine quartz sand into the centre of a U-tube so that it formed a porous diaphragm, then he filled the tube with water and applied electric current to the electrodes in both arms of the tube (Fig. 7.2). The water level in the arm having a negative electrode rose until the level difference in both arms attained a definite value. This process, like electrophoresis, occurs at a constant rate; the amount of liquid transferred is directly proportional to the potential gradient applied and the dielectric constant, and inversely proportional to the viscosity of the medium. As was established by G. Wiedemann's investigations in 1852, the amount of liquid passing through the capillaries of a porous diaphragm is proportional to current intensity, and does not depend on the sectional area or the diaphragm thickness at constant current. This phenomenon was called *electroosmosis* or *electroendoosmosis.*

Both phenomena discovered by Reuss are caused by the fact that the solid and liquid phases carry opposite charges. In electrophoresis, the negatively charged dispersed phase is transferred to the positive electrode because electric field exists between electrodes and since clay particles are small. In electroosmosis, since sand particles are too heavy, positively charged liquid moves to the negative electrode along capillaries in the sand layer under the action of the electric field.

Two phenomena which seem to be the opposite of electrophoresis and electroosmosis were discovered later. In 1878, Dorn discovered that when particles sediment in a liquid, e.g., sand in water, an electromotive force originates between two electrodes inserted in different places of a liquid column. This phenomenon which is the opposite of electrophoresis has become known as the *Dorn effect* or the *sedimentation potential.*

It was also found out that the potential gradient is established when a liquid is pressed through a porous partition which has electrodes on both sides. This phenomenon, which G. Quincke discovered in 1859 and which is the opposite of electroosmosis was called the *streaming potential.*

These four phenomena are known as *electrokinetic phenomena* because they involve movement of a liquid or particles when the potential gradient is applied, or, conversely, the establishment of the potential gradient when a liquid or particles move. These phenomena, being connected with the presence of an interface, are exhibited most readily in highly dispersed systems having a large specific surface.

Let us consider electrophoresis and electroosmosis in greater detail because they are important in studying and understanding the electrical properties of colloidal systems.

All the electrokinetic phenomena are caused by the opposite charges of a solid and a liquid. This principle was acknowledged by Quincke and Helmholtz as early as the latter half of the 19th century. However, it turned out to be far more difficult to explain why these charges originate at the interface.

As was first believed, the charge of colloidal particles is caused by the transport of electrons from one phase to another when two phases are in contact. However, if this viewpoint were correct, Kohn's rule should be obeyed in electrophoresis: according to the rule, bodies having a larger dielectric constant should be charged positively because they are electron donors, and bodies having a smaller dielectric constant should be charged negatively because they are acceptors of electrons. The rule seems to be observed for some colloidal systems, such as sulphur hydrosols or emulsions of oil in water. However, it is inapplicable for a large class of colloidal solutions of metals and their oxides in water. Metal particles having an infinitely large dielectric constant carry, as a rule, a negative charge whereas water which has a small dielectric constant in comparison with them is charged positively. Moreover, the charge of a colloidal particle can become opposite under the action of very small quantities of some electrolytes which do not noticeably affect the dielectric constant of a medium. These observations have shown that the theory connecting the origin of a charge with the contact between two phases was untenable.

From the modern viewpoint, the charge on the colloidal particles of lyosols, which is exhibited in electrophoresis, is caused by the presence on their surface of an electric double layer of ions that originates either upon the selective adsorption of one of the ions of an electrolyte in a solution or owing to the ionization of the surface molecules of substances. This viewpoint is supported by the fact that electrokinetic phenomena either are not observed at all or are almost not observed in liquid media having a very small dielectric constant, in which electrolytes do not noticeably dissociate. Such liquids are chloroform, diethyl ether, and carbon disulphide. At the same time, electrokinetic phenomena are observed in nitrobenzene and such weakly polar liquids as acetone, ethyl and methyl alcohols, and especially water.

The formation of an electric double layer upon the selective adsorption of an ion has been considered in Chap. 6. Fig. 7.3 shows, in the most general form, an electric double layer that originates on crystals of silver iodide which are in a weak solution of potassium iodide. Iodide ions (*potential-determining ions*) complete the construction of the crystal lattice of silver iodide and thus charge the parti-

cles negatively whereas potassium ions (*counterions*) are in the solution near the interface.* On the whole, the entire complex, known as the *micelle*, is electroneutral.

In fact, an electric double layer can be formed as a result of the selective adsorption of one of the ions present in the dispersion medium even when there is no completion of the crystal lattice. For

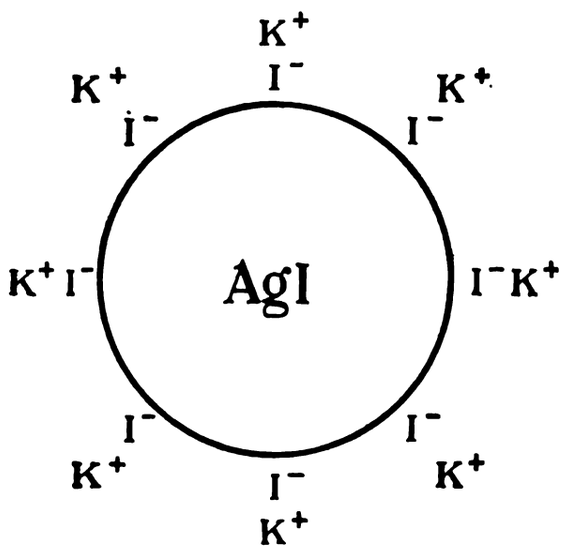

Fig. 7.3. Diagram of the formation of the electric double layer around a particle of silver iodide in a solution of potassium iodide

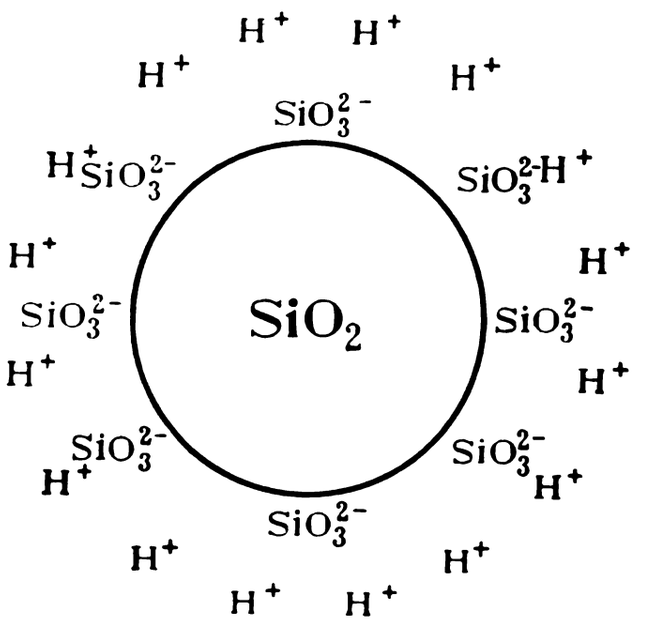

Fig. 7.4. Diagram of the formation of the electric double layer around a particle of silicon dioxide in water

example, an electric double layer is formed on particles of paraffin which is dispersed in a weak alkaline solution, owing to the selective adsorption of the hydroxyl ion which under the given conditions is adsorbed better than the ion of alkali metal.

The origin of an electric double layer owing to ionization can be illustrated by the formation of this layer on particles of an aqueous sol of silicon dioxide. The molecules of SiO_2 which are on the surface of such particles interact with the dispersion medium, are hydrated, and form silicic acid which can be ionized:

$$H_2SiO_3 \rightleftarrows SiO_3^{2-} + 2H^+$$

* The crystal AgI which has a cubic shape is schematically represented as a circle in Fig. 7.3. For the sake of simplicity, we will also do this in similar cases later. Potential-determining ions here are shown outside the particle. In some textbooks, these ions are put directly in the surface layer of the particle. Each way of distributing potential-determining ions has its advantages. The former way shows that the potential-determining ion in most cases is adsorbed by the particle from the external medium. The latter way indicates that the adsorbed potential-forming ion has completed the construction of the particle and become a part of it. Since neither of these ways has any clear advantages, we will hereafter use the former because it is accepted in most Soviet textbooks as well as in the first Russian edition of this book.

In this case, the silicate ions SiO_3^{2-} remain on the surface of a particle, so that it is charged negatively, while hydrogen ions pass over to the solution. The electric double layer on the surface of SiO_2 particles is schematically illustrated in Fig. 7.4. Of course, the entire complex is electroneutral. It is quite likely that not all the molecules

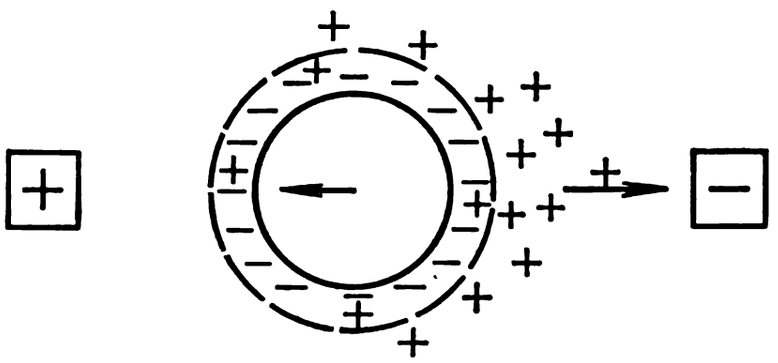

Fig. 7.5. Diagram of the motion of a colloidal particle and counterions in electrophoresis

of H_2SiO_3 on the surface are ionized. There may be also single-stage dissociation into the ions $HSiO_3^-$ and H^+. But this does not essentially change anything.

The formation of an electric double layer on colloidal particles is considered in greater detail in the next chapter.

When an electric field acts on particles carrying an electric double layer, a phenomenon similar to electrolysis occurs. If the dispersed phase is charged negatively, the colloidal particles together with the negative potential-determining ions adsorbed on them move to the anode, while the positively-charged counterions, to the cathode. If the dispersed phase is charged positively, particles and ions move in the opposite direction. Only a part of the counterions moves to the electrode whose charge is the same as that of the charged particles. The other part of the counterions which are very close to the surface of the dispersed phase is bound to the particles by comparatively strong electric and adsorption forces, and is forced to move together with them. Electrophoresis can be explained by a scheme illustrated in Fig. 7.5. In this case, it is assumed that the potential-determining ions are charged negatively, and the counterions, positively. Of course, electrophoresis is not a simple transfer of charged particles and counterions to the appropriate electrodes; it is accompanied by constant exchange between the counterions of neighbouring colloidal particles. In this respect, electrophoresis completely resembles electrolysis which involves the exchange of the ions of neighbouring molecules.

It seems that the given concept of electrophoresis is contradicted by observations made earlier which show that, in electrophoresis, the colloidal substance, rather than the ions, is transferred. But it

is only an apparent contradiction because a negligible amount of an electrolyte which is very difficult to determine quantitatively is required for an electric double layer to be formed on particles. For example, it was discovered that in obtaining the sol of arsenic sulphide which is stabilized by the hydrogen sulphide molecules, for 0.67 g of As_2S_3 deposited on the anode, there is only 10^{-5} g of H_2 deposited on the cathode. Of course, such an amount of hydrogen cannot be

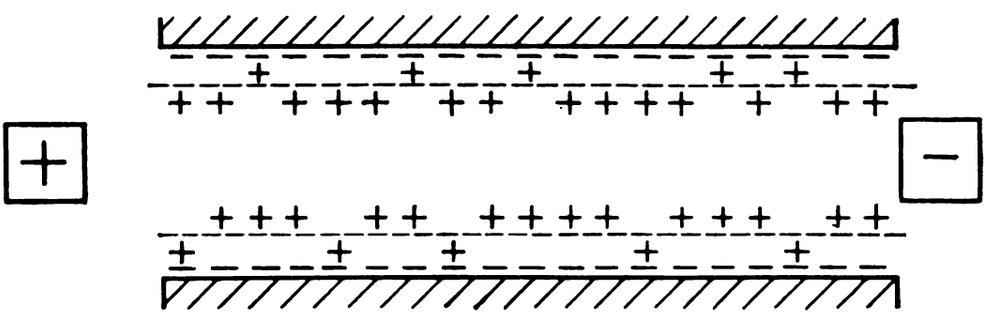

Fig. 7.6. Diagram of the motion of a liquid and counterions in electroosmosis

determined by ordinary analytical methods, and this gave rise earlier to incorrect concepts that only the colloidal substance, and not the ions, is transferred in electrophoresis.

Electroosmosis is explained in a similar way. In this case, the electric double layer is formed in the internal surface of capillaries of a porous body owing either to the selective adsorption of one of the ions of an electrolyte present in the liquid that fills up a capillary, or to the ionization of molecules of the substance out of which the capillary wall is made, or to the adsorption of the ions OH^- or H^+, which are always present in water, on the capillary surface.

Fig. 7.6 represents an electric double layer formed in a capillary, and it is assumed that the potential-determining ions are charged negatively, whereas the counterions, positively. When an electric field is applied to a capillary by introducing electrodes into the vessels which the capillary connects, the layer of counterions in it moves parallel to the stationary layer of the potential-determining ions towards the cathode; this causes the liquid filling the capillary to move towards the cathode under the action of forces of friction and molecular cohesion. The counterion places that have become vacant are immediately filled up with cations which are present in the volume of the liquid that fills up the capillary while the ions that correspond to these cations move towards the anode (Fig. 7.6 does not show the ions which are in the volume of the liquid that fills up the capillary).

We will deal with electrophoresis and electroosmosis again at the end of this chapter when we consider the quantitative aspect of both phenomena.

2. STRUCTURE OF THE ELECTRIC DOUBLE LAYER

To simplify exposition, we will mainly consider the flat electric double layer, although such a layer is hardly found in colloidal solutions and fine-porous bodies. Such a simplification can be made when the thickness of the double layer is small in comparison with the radius of curvature of the surface of colloidal particles or capillaries.

Moreover, in considering the electric double layer, let us take account of the following general principles on which all theories of its structure are based. The electric double layer consists of ions of the same sign that are relatively firmly bound to the dispersed solid phase in the case of lyosols (potential-determining ions), and an equivalent amount of the oppositely charged ions that are in the liquid dispersion medium near the interface (counterions). The charge on the surface of the solid phase is believed, as the first approximation, to be uniformly distributed along the surface. There is dynamic equilibrium between the counterions and the free ions (which are not in the electric double layer) of the same sign in the liquid. The dispersion medium is always a continuous phase whose effect on the electric double layer is determined only by its dielectric constant.

With such prerequisites, the theories of the structure of the electric double layer differ from one another mainly in the interpretation of the counterion layer structure.

Helmholtz-Perrin theory. According to this theory, the electric double layer is a flat condenser, as it were, one plate of which is connected directly to the surface of a solid (a wall) whereas the other plate which carries the opposite charge is in a liquid at a very small distance away from the first plate. The potential in such a double layer, like that in the plane condenser, should apparently fall very sharply (along the straight line), and the value of the surface charge density σ will be determined by the formula

$$\sigma = \frac{\varepsilon}{4\pi\delta}\varphi_0 \tag{7.1}$$

where ε = absolute dielectric constant of the medium that fills up the space between the condenser plates;
φ_0 = potential difference between the dispersed phase and the solution;
δ = distance between the plates.

Fig. 7.7 schematically illustrates the structure of such an electric double layer: the crosshatched part is the solid phase, and the remaining part is the solution; positive and negative ions forming

the double layer are denoted by "+" and "—", respectively. Free ions of an electrolyte which are always present in a liquid are not shown so as not to complicate the illustration. The potential falls as the distance x from the surface of the solid body grows; the total potential jump in such a double layer is at the same time a jump in potential between the solid phase and the solution.

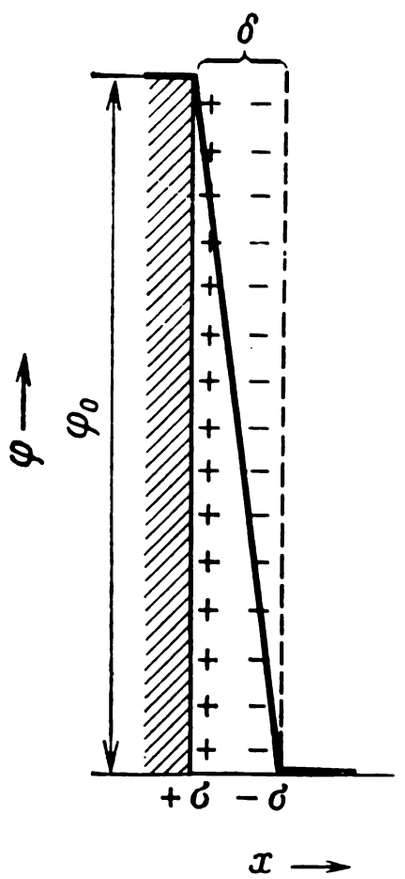

Fig. 7.7. Electric double layer according to Helmholtz and Perrin and the potential jump in it

The given illustration of the structure of the electric double layer does not explain several features of electrokinetic phenomena. At present, it is only of historical importance to colloid chemistry. The main shortcoming of the illustration is the fact that the thickness of the Helmholtz-Perrin double layer is very small and approximates molecular dimensions. At the same time, hydrodynamic investigations have shown that the place of discontinuity (slipping plane) is always in the liquid phase at a comparatively great distance away from the interface when the solid and liquid phases move relative to each other. The thickness of the liquid layer that has "adhered" to the solid surface under these conditions is in any case greater than the thickness of the Helmholtz-Perrin electric double layer.

If the Helmholtz-Perrin theory were correct, the Dorn effect or the streaming potential should not be observed when colloidal particles sediment in a liquid or when the liquid is pressed through a capillary, also electrophoresis and electroosmosis would be impossible. However, even if we assume that, as it has been done earlier, the slipping plane is between the two plates of the electric double layer, the Helmholtz-Perrin concepts create a contradiction. Indeed, if such an allowance is made, the *electrokinetic potential* of electrophoresis should correspond to the potential difference between all the potential-determining ions and all the counterions, i.e., it should be equal to the total potential jump. However, the electrokinetic potential is, as a rule, smaller than the total potential jump, and changes quite differently under the action of various factors. For example, the total potential jump does not depend, to any considerable extent, on indifferent electrolytes that do not contain ions which

are capable of completing the construction of the crystal lattice; at the same time, such electrolytes greatly affect the electrokinetic potential.

The foregoing exposition shows that the total potential jump and the electrokinetic potential are different quantities, and therefore Helmholtz's and Perrin's concepts of the flat electric layer are not enough for explaining electrokinetic phenomena.

Gouy-Chapman theory. A significant step forward was the theory of the electric double layer with a diffuse counterion layer, proposed independently by Gouy (1910) and Chapman (1913). This theory eliminated many of the shortcomings of the Helmholtz-Perrin theory. According to the Gouy-Chapman theory, counterions cannot concentrate only at the interface and form a monoionic layer, but are scattered in the liquid phase at a certain distance away from the interface. Such a structure of the double layer is determined, on the one hand, by the electric field of a solid phase which attracts an equivalent amount of oppositely charged ions as close as possible to the wall, and, on the other, by the thermal motion of ions as a result of which counterions scatter in the liquid volume.

The action of the electric field prevails in the immediate proximity of the interface. As the distance from the interface increases, the intensity of the field gradually decreases and counterions of the dou ble layer scatter more and more owing to thermal motion, as a result, the concentration of counterions diminishes and becomes equal to that of ions which are in the bulk of liquid. That is how the equilibrium diffuse layer of counterions, which are connected with the solid, originates. Of course, the equilibrium of this layer is dynamic.

On the other hand, the ions in the liquid that bear the same sign as the potential-determining ions adsorbed by the wall are repulsed from the solid phase by electric forces and go deep into the solution. This causes the distribution of potential-determining ions and counterions in the diffuse part of the electric double layer, as is illustrated in Fig. 7.8.

The structure of the electric double layer according to Gouy and Chapman and the potential drop in it are schematically illustrated in Fig. 7.9. The potential drop follows not a straight line, but a curve, because the counterions which compensate the wall charge are distributed non-uniformly. The curve drops steeper in places where there are more compensating counterions, and, conversely, it is smoother in places where there is a small amount of compensating counterions.

Since the extent of diffusion of the counterion layer is determined by thermal scattering, all the counterions should be at the solid surface at a temperature of absolute zero. Consequently, the theore-

tical concepts of Helmholtz and Perrin turn out to be a particular case of the Gouy-Chapman theory.

The equilibrium distribution of ions established at the solid wall is similar to that of gas molecules established in the atmosphere under the action of gravity, the only difference is that the gravitational field does not depend on the distribution of molecules whereas,

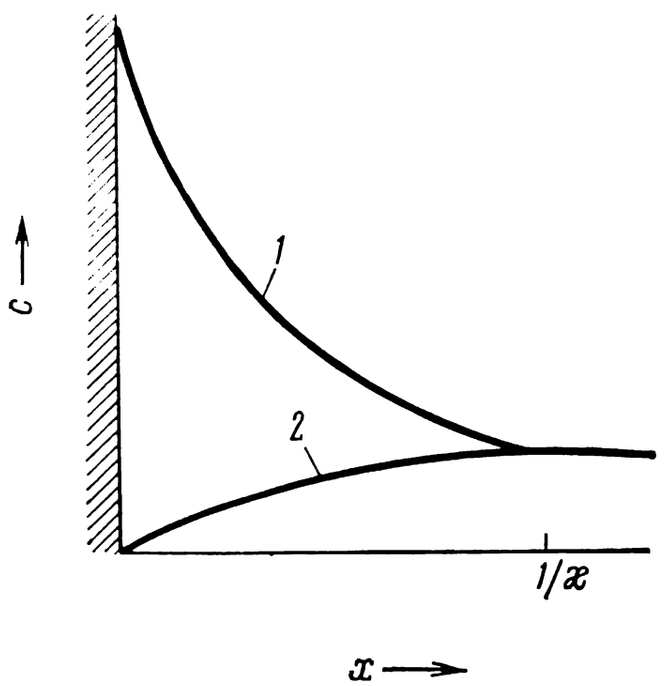

Fig. 7.8. Dependence of the concentration c of counterions (curve *1*) and potential-determining ions (curve *2*) on the distance x from the plane wall ($1/\varkappa$ is the thickness of the electric double layer)

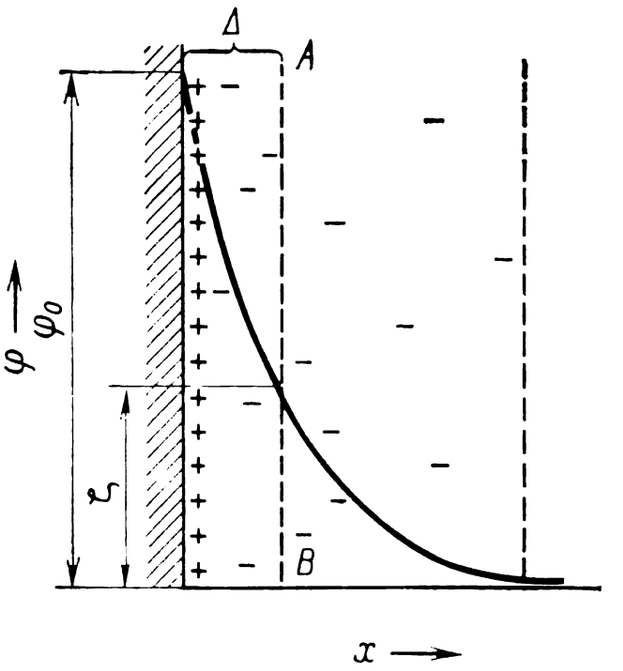

Fig. 7.9. Electric double layer according to Gouy and Chapman and the potential drop in it

in the case of the electric double layer, the electric field is a function of the distribution of charged ions. The number of counterions at the charged surface of a solid phase decreases according to the Boltzmann distribution law as the distance from the interface into the solution grows whereas the number of potential-determining ions increases according to the same law. It thus follows that if the concentration of positive and negative ions in a point, whose potential is φ_x, is denoted by c_+ and c_- (in moles per unit volume), then for distance $x = \infty$

$$c_+ = c_- = c_\infty \tag{7.2}$$

and for a distance x which is not too great

$$c_+ = c_\infty \exp\left(-Fz\varphi_x/RT\right) \tag{7.3}$$

$$c_- = c_\infty \exp\left(Fz\varphi_x/RT\right) \tag{7.4}$$

where c_∞ = electrolytic concentration at an infinitely great distance from the solid phase at $\varphi_\infty = 0$;
F = Faraday number (96,540 coulombs);
z = valency of the ion;
R = gas constant;
T = absolute temperature.

According to the Boltzmann distribution equation, the product $Fz\varphi_x$ in the exponential factor of Eqs. (7.3) and (7.4) is the electric work of transfer of one mole of the appropriate type of ions from the volume of the solution (where $\varphi = 0$) to the point having the potential of φ_x.

It is clear that, at $x = \infty$, $\varphi_x = \varphi_\infty = 0$ and, at $x = 0$, $\varphi_x = \varphi_0$, i.e., the potential is equal to zero at an infinitely great distance away from the interface, and is equal to the total surface potential jump at the interface.

The concepts evolved by Gouy and Chapman explain some electrokinetic phenomena. For example, since the slipping plane AB, when the solid and liquid phases move relative to one another, lies in the liquid at a small distance Δ away from the interface where the potential still does not drop to that of the liquid (see Fig. 7.9), the difference between it and the potential in the liquid in this place corresponds to the charge of this part of the diffuse layer. It is this potential that determines the movement of phases when the electric field is applied, i.e., the potential causes electrophoresis or electroosmosis. The electrokinetic potential, or, as it is often called, the *ζ-potential*, is a part of the total jump of potential φ_0. Hence, it is clear why the electrokinetic potential differs from zero, but is not equal to the total potential jump. Moreover, the structure of the electric double layer proposed by Gouy and Chapman explains why different factors affect the two potentials differently.

Let us see, for example, how the introduction of an indifferent electrolyte into a system affects both of these potentials. In this case, the total potential jump barely changes. Things are quite different with the electrokinetic potential. As the concentration of the electrolyte being introduced increases, the thickness of the diffuse layer decreases because the same (equivalent) number of charges of the opposite sign is always required for compensating the potential-determining ions. The electric double layer is said to contract. As a result, the distribution of the potential in it also changes. Moreover, there will be a change in the ζ-potential which corresponds to the slipping plane of a liquid in electrophoresis or electroosmosis.

The change in the ζ-potential when ever increasing quantities of an indifferent electrolyte are introduced is shown in Fig. 7.10. When the concentrations of the electrolyte are large enough, the diffuse layer may contract to a monoionic layer, and the electric double

layer thus becomes the Helmholtz-Perrin layer. Of course, ζ-potential will be equal to zero because this layer will be closer than the slipping plane to the wall.

The Gouy-Chapman theory is based on the same physical concepts as the Debye-Hückel theory of strong electrolytes, incidentally, the former originated earlier than the latter.

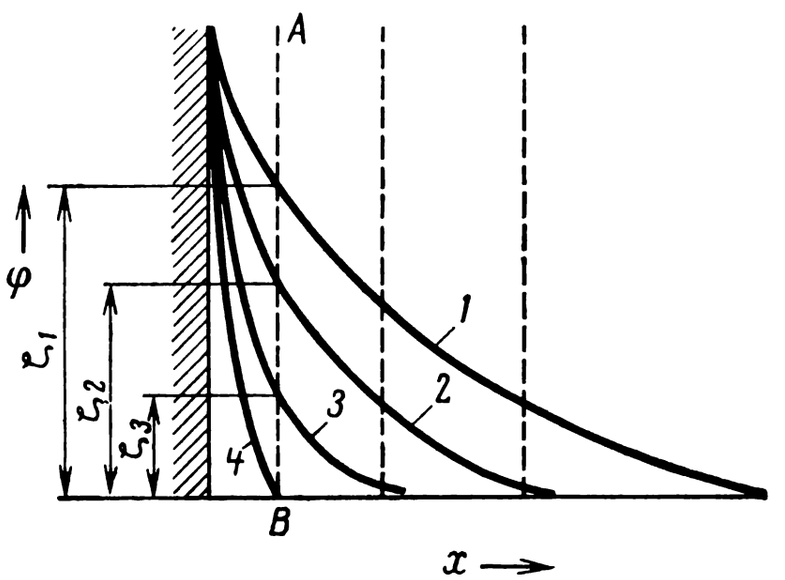

Fig. 7.10. Effect of an indifferent electrolyte on both the thickness of the electric double layer and the electrokinetic potential (the amount of the electrolyte increases from curve *1* to curve *4*)

According to the strong electrolyte theory, the thickness of the ionic atmosphere $1/\varkappa$ is determined by the equation

$$\frac{1}{\varkappa}=\sqrt{\frac{\varepsilon kT}{8\pi e^2 N_A \sum c_i z_i^2}}=\sqrt{\frac{\varepsilon RT}{8\pi e^2 N_A^2 \sum c_i z_i^2}}=\sqrt{\frac{\varepsilon RT}{8\pi F^2 \sum c_i z_i^2}} \quad (7.5)$$

where ε = absolute dielectric constant of the liquid;
k = Boltzmann constant;
T = absolute temperature;
e = electron charge;
N_A = Avogadro number;
c_i = bulk concentration of different ions;
z_i = valency of different ions;
R = gas constant;
F = Faraday number.

Eq. (7.5), which connects $1/\varkappa$, c_i and z_i, can be simplified to

$$\frac{1}{\varkappa}=k\frac{1}{\sqrt{\sum c_i z_i^2}}$$

where k = equation constant.

It follows from the given equation that the ionic atmosphere should be the smaller, the higher is the concentration of ions in the solution and the greater is their valency. Naturally, a similar correlation is also maintained when the ionic atmosphere is formed not around the ion, but near the interface. However, it is only at small surface potentials that the value of the ζ-potential is determined merely by the thickness of the ionic atmosphere, and it is only under these conditions that it will be equally affected by the charges of counterions and those of secondary ions which are present in a system. As theory shows, when surface potentials are high (over 50 mV), the decrease in the ζ-potential is affected much more strongly by the charge of a counterion, especially when it is large. The physical meaning of this phenomenon is that a strongly charged counterion of an electrolyte is attracted to the surface and greatly screens it. The growth in the ability of the counterion to reduce the ζ-potential with an increase in its valency can be clearly seen from the following experimental data:

Counterion valency	IV	III	II	I
c_ζ	1	10-20	60-100	500-1000

In this case, the value of c_ζ is the relative counterion concentration that is required for reducing the electrokinetic potential to the same value, such as 50 mV. As we see, this series does not give any exact relationships. In fact, this cannot be expected because the ability of the ion to compress the electric double layer depends not only on its valency, but also on its size, polarizability, the ability to be hydrated, and so forth. Proceeding from Gouy's and Chapman's concepts, Müller showed purely mathematically that the ability of counterions to reduce the ζ-potential should grow rapidly with their valency; in addition, for a flat interface, he calculated the series

Counterion valency	IV	III	II	I
c_ζ	1	7.5	57	540

This is in good agreement with experimental data.

Let us now consider the quantitative aspect of the Gouy-Chapman theory.

One of the principal initial equations in this theory is the Poisson equation which connects ρ, the volume density of a charge, and the potential φ:

$$\nabla^2\varphi = -4\pi\rho/\varepsilon \qquad (7.6)$$

where ε = absolute dielectric constant;

∇^2 = shortened notation of the Laplacian operator

$$\nabla^2\varphi = (\partial^2\varphi/\partial x^2) + (\partial^2\varphi/\partial y^2) + (\partial^2\varphi/\partial z^2) \qquad (7.7)$$

When the solid surface is flat, the potential changes only along the normal to the surface, and the derivatives of y and z are thus equal to zero. In this particular case, the dependence of the potential on x, the distance to the wall, is expressed by the equation

$$d^2\varphi/dx^2 = -4\pi\rho/\varepsilon \tag{7.8}$$

Apparently, at $x = \infty$

$$\varphi = 0;\ d\varphi/dx = 0, \text{ and } \rho = 0$$

while at $x = 0$

$$\varphi = \varphi_0 \text{ and } d\varphi/dx = -4\pi\sigma/\varepsilon$$

where φ_0 = potential of the interface;
σ = charge (surface density of electricity) of the same interface.

The volume density of the charge can be represented as

$$\rho = Fz\,(c_+ - c_-) \tag{7.9}$$

where F = Faraday number;
z = valency of ions;
c_+ and c_- = concentration of positive and negative ions, mol/l.

Eq. (7.9) is apparently applicable only to the binary symmetrical electrolyte. In other cases, the formula should have the form of an algebraic sum

$$\rho = \sum Fz_i c_i \tag{7.10}$$

However, we will not consider this more complicated case here.

Substituting Eqs. (7.3) and (7.4) in Eq. (7.9), we obtain

$$\rho = Fzc_\infty\,[\exp(-Fz\varphi/RT) - \exp(Fz\varphi/RT)] \tag{7.11}$$

If the value of ρ is substituted in Eq. (7.8) we may obtain

$$\frac{d^2\varphi}{dx^2} = -\frac{4\pi}{\varepsilon} Fzc_\infty \left[\exp\left(-\frac{Fz\varphi}{RT}\right) - \exp\left(\frac{Fz\varphi}{RT}\right)\right] \tag{7.12}$$

To perform the first integration and obtain the derivative $d\varphi/dx$, let us transform the equation obtained in the following way:

$$\frac{d^2\varphi}{dx^2} = \frac{d\,(d\varphi/dx)}{dx} = -\frac{4\pi}{\varepsilon} Fzc_\infty \left[\exp\left(-\frac{Fz\varphi}{RT}\right) - \exp\left(\frac{Fz\varphi}{RT}\right)\right]$$

$$d\left(\frac{d\varphi}{dx}\right) = -\frac{4\pi}{\varepsilon} Fzc_\infty \left[\exp\left(-\frac{Fz\varphi}{RT}\right) - \exp\left(\frac{Fz\varphi}{RT}\right)\right] \frac{dx}{d\varphi} d\varphi$$

$$\frac{d\varphi}{dx} d\left(\frac{d\varphi}{dx}\right) = -\frac{4\pi}{\varepsilon} Fzc_\infty \left[\exp\left(-\frac{Fz\varphi}{RT}\right) - \exp\left(\frac{Fz\varphi}{RT}\right)\right] d\varphi$$

Let us integrate the expression obtained from 0 to φ. Taking into account that at $\varphi \to 0$ $d\varphi/dx \to 0$, we have

$$\left(\frac{d\varphi}{dx}\right)^2 = \frac{8\pi}{\varepsilon} Fzc_\infty \int_0^\varphi \left[\exp\left(\frac{Fz\varphi}{RT}\right) - \exp\left(-\frac{Fz\varphi}{RT}\right)\right] d\varphi =$$

$$= \frac{8\pi}{\varepsilon} c_\infty RT \int_0^\varphi \left[\exp\left(\frac{Fz\varphi}{RT}\right) - \exp\left(-\frac{Fz\varphi}{RT}\right)\right] d\frac{Fz\varphi}{RT}$$

$$\left(\frac{d\varphi}{dx}\right)^2 = \frac{8\pi}{\varepsilon} c_\infty RT \left[\exp\left(\frac{Fz\varphi}{RT}\right) + \exp\left(-\frac{Fz\varphi}{RT}\right) - 2\right] =$$

$$= \frac{8\pi}{\varepsilon} c_\infty RT \left[\exp\left(\frac{Fz\varphi}{2RT}\right) - \exp\left(-\frac{Fz\varphi}{2RT}\right)\right]^2$$

or

$$\frac{d\varphi}{dx} = \pm \sqrt{\frac{8\pi RTc_\infty}{\varepsilon}} \left[\exp\left(\frac{Fz\varphi}{2RT}\right) - \exp\left(-\frac{Fz\varphi}{2RT}\right)\right]$$

Since the quantity φ decreases when x increases, the derivative $d\varphi/dx$ is negative, and we finally obtain

$$\frac{d\varphi}{dx} = -\sqrt{\frac{8\pi RTc_\infty}{\varepsilon}} \left[\exp\left(\frac{Fz\varphi}{2RT}\right) - \exp\left(-\frac{Fz\varphi}{2RT}\right)\right] \quad (7.13)$$

This equation allows us to draw several conclusions. If an electrolyte, whose concentration in a solution is c_∞, is an indifferent one, i.e., if it does not contain potential-determining ions, the potential φ_0 which is equal to the total potential jump does not depend on c_∞. Consequently, according to Eq. (7.13), only the inclination of the curve $\varphi = f(x)$ changes with c_∞ while the value of φ_0 remains constant. Fig. 7.10 shows a family of curves $\varphi = f(x)$; the value of φ_0 is the same whereas $d\varphi/dx$ grows, in conformity with Eq. (7.13), from curve *1* to curves *2*, *3*, *4* at different c_∞. Since the slipping plane in Fig. 7.10 corresponds to the line AB, the initial electrokinetic potential ζ_1 decreases with an increase in electrolytic concentration and assumes the values of ζ_2, ζ_3, and so forth. When the counterionic valency is greater than unity, taking into account Eq. (7.13), the derivative $d\varphi/dx$ should increase more sharply with concentration, i.e., the electrokinetic potential will fall more steeply.

Hence, the Gouy-Chapman theory explains well a decrease in the ζ-potential when the concentration of the counterion and its valency increase.

At small φ_0 and, accordingly, at values of $Fz\varphi_0/(2RT) \ll 1$, we may use the approximation $e^\alpha = 1 + \alpha$ and $e^{-\alpha} = 1 - \alpha$; this gives $e^\alpha - e^{-\alpha} = 2\alpha$. Then, instead of Eq. (7.13), we will obtain an approx-

imate equation

$$\frac{d\varphi}{dx} = -\sqrt{\frac{8\pi RTc_\infty}{\varepsilon}} \cdot \frac{Fz\varphi}{RT} = -\sqrt{\frac{8\pi F^2 z^2 c_\infty}{\varepsilon RT}}\,\varphi = -\varkappa\varphi$$

where

$$\varkappa = \sqrt{\frac{8\pi F^2 z^2 c_\infty}{\varepsilon RT}} = \sqrt{\frac{8\pi e^2 z^2 N_A c_\infty}{\varepsilon kT}} \qquad (7.14)$$

Integrating Eq. (7.14) and taking into account that at $x = 0$ $\varphi = \varphi_0$, we obtain

$$\varphi = \varphi_0 e^{-\varkappa x} \qquad (7.15)$$

Eq. (7.15) shows that the potential decreases by $e = 2.72$ times at a distance of the order of $1/\varkappa$*.

Eq. (7.13) makes it possible to establish the correlation between σ, the density of the surface charge at the interface, and the surface potential φ_0. It follows from the condition of electroneutrality of the electric double layer that the surface charge by its absolute value is equal to the total volume charge in the solution, i.e.,

$$\sigma = -\int_0^\infty \rho\, dx \qquad (7.16)$$

Using the Poisson equation (7.8), this equation can be integrated to yield

$$\sigma = +\int_0^\infty \frac{\varepsilon}{4\pi}\frac{d^2\varphi}{dx^2}\,dx = -\frac{\varepsilon}{4\pi}\left(\frac{d\varphi}{dx}\right)_{x=0} \qquad (7.17)$$

Replacing $d\varphi/dx$ by the value found for this derivative in Eq. (7.13), we obtain

$$\sigma = \sqrt{\frac{\varepsilon RTc_\infty}{2\pi}}\left[\exp\left(\frac{Fz\varphi_0}{2RT}\right) - \exp\left(-\frac{Fz\varphi_0}{2RT}\right)\right] \qquad (7.18)$$

Using the simplification similar to the one employed in the derivation of Eq. (7.14), the following approximate expression can be obtained from Eq. (7.18) when the values of φ_0 and $Fz\varphi_0/2RT$ are small:

$$\sigma = \sqrt{\frac{\varepsilon RTc_\infty}{2\pi}} \cdot \frac{Fz\varphi_0}{RT} = \frac{\varepsilon}{4\pi}\sqrt{\frac{8\pi F^2 z^2 c_\infty}{\varepsilon RT}} \cdot \varphi_0 = \frac{\varepsilon\varkappa}{4\pi}\varphi_0 \qquad (7.19)$$

* The quantity $1/\varkappa$ which in the theory of strong electrolytes is called the radius of the ionic atmosphere (or the Debye radius) cannot be interpreted geometrically as the radius of a sphere outside of which the action of the field of the ion under consideration becomes zero. Strictly speaking, the physical quantity of the radius of the ionic atmosphere is infinite. However, the field potential decreases exponentially with an increase in the distance from the ion being considered; the effect of this potential can be neglected at a distance which is much greater than $1/\varkappa$.

where

$$\varkappa = \sqrt{\frac{8\pi F^2 z^2 c_\infty}{\varepsilon RT}} = \sqrt{\frac{8\pi e^2 z^2 N_A c_\infty}{\varepsilon kT}}$$

In this case, the charge and potential at the interface are proportional to each other, and the electric double layer acts as a plane condenser, the distance between whose plates is equal to $1/\varkappa \approx \delta$. The fact that the distance between the condenser plates, equivalent to the double layer, is equal approximately to $1/\varkappa$ justified the expression "the thickness of the electric double layer is equal to $1/\varkappa$".

An important property of the electric double layer which can be easily characterized quantitatively is its *differential* (and *integral*) *capacities*

$$\partial\sigma/\partial\varphi_0 \text{ and } \sigma/\varphi_0 \qquad (7.20)$$

For small potentials, the differential and integral capacities are equal to the same quantity C which can be calculated by the equation

$$C = \sigma/\varphi_0 = \varepsilon\varkappa/(4\pi) \qquad (7.21)$$

For higher potentials, the capacity of the electric double layer becomes greater than this quantity.

At room temperature and $z = 1$, the value of $\varkappa$ is equal to approximately $3 \times 10^7\sqrt{c}$ (where c is the electrolyte concentration, mol/l). Hence, the theoretical capacity of the electric double layer is $3 \times \times 10^7 \times 80/4 = 200$ μF/cm^2 in 1 N aqueous electrolyte solution containing monovalent cations and anions. The empirical capacities are equal only to one-tenth of this value.

The untenability of the Gouy-Chapman theory can be shown also in another way. If an electrolytic solution is not too dilute (say 0.1 N) and the potential near the wall is high (for example, 200 mV), for the theoretical and empirical values of capacity to coincide, the counterion concentration near the wall should be 300 N, and this is impossible. The experimentally and theoretically found values of capacity of the electric double layer differ because the Gouy-Chapman theory does not take the dimensions of ions into account and regards them as point charges which can closely approach the wall; this determines the higher values of theoretical quantities as compared to empirical ones.

Another shortcoming of the Gouy-Chapman theory is that it does not explain the *reversal of charge*, i.e., a change in the sign of the electrokinetic potential when an electrolyte having a polyvalent ion whose charge is opposite in sign to that of the dispersed phase is introduced into a system.

Furthermore, the Gouy-Chapman theory does not explain why different counterions of the same valency produce different action on the electric double layer. According to the theory, the introduction

of an equivalent amount of different counterions of the same valency should compress the electric double layer and reduce the ζ-potential to the same extent. However, experiments show that this is not so. The effectiveness of the action of ions of the same valency on the electric double layer grows with the ionic radius.

The Gouy-Chapman theory is relatively well applicable to sufficiently diluted colloidal solutions, but not to concentrated ones.

All these difficulties are overcome to a considerable extent in the theory of the structure of the electric double layer proposed by Stern.

Stern's theory. In 1924, Stern proposed a scheme for the structure of the electric double layer in which he combined the Helmholtz-Perrin and Gouy-Chapman schemes. In elaborating the theory of the electric double layer, Stern used two prerequisites. First, he presumed that ions have certain finite dimensions and consequently ionic centres cannot be closer to the solid surface by a distance smaller than the ionic radius. Secondly, Stern took account of the specific, non-electric interaction of ions with the solid surface. This interaction is caused by a field of molecular (adsorption) forces at a small distance away from the surface. As we will see when we discuss the causes of the stability and coagulation of colloidal systems, the molecular forces which act between bodies consisting of many molecules are long-range ones owing to their additivity. However, when ion interacts with the solid surface, their action rapidly decreases with distance and therefore should be taken into account only at the very surface of a solid (at a distance of several angstroms).

According to Stern, the first layer or even the first several layers of counterions are attracted to the wall under the action of both electrostatic and adsorption forces. As a result, a part of counterions is retained by the surface at a very close distance which is of the order of one-two molecules, forming a plane condenser having a thickness of δ, as envisaged by the Helmholtz-Perrin theory. This layer in which the electric potential falls sharply is termed the *Helmholtz layer*, or the *Stern layer*, or the *adsorption layer*. The remaining counterions which are needed for compensating the potential-determining ions form, as a result of thermal scattering, a diffuse part of the double layer; they are distributed in it according to the same laws as in the diffuse Gouy-Chapman layer. This part of the double layer in which the potential falls gradually is sometimes called the *Gouy layer*. The scheme of the electric double layer according to Stern and the electric potential drop in it are illustrated in Fig. 7.11.

It follows from the illustration that the total potential drop φ_0 consists of the potential drop φ_δ in the diffuse part of the double layer

and the difference in potentials ($\varphi_0 - \varphi_\delta$) between the condenser plates. It still remains unclear where the slipping plane is in such a layer. Some authors believe that it coincides with the boundary between the Helmholtz layer and the Gouy layer. However, in general, we may suppose it to be in the Gouy layer, as is represented in Fig. 7.11 (the slipping plane is denoted by the dotted line AB). Hence, the potential at the boundary between the Helmholtz layer and the Gouy layer must not necessarily be equal to the ζ-potential.

Of course, when electrolytes are introduced into a system, the diffuse layer will contract and an increasing number of counterions will appear into the adsorption layer. According to Stern, the electric double layer in this case draws closer and closer to the layer envisaged in the Helmholtz-Perrin theory, while the ζ-potential decreases, gradually approaching zero. Conversely, when a system is diluted the diffuse layer expands and the ζ-potential grows.

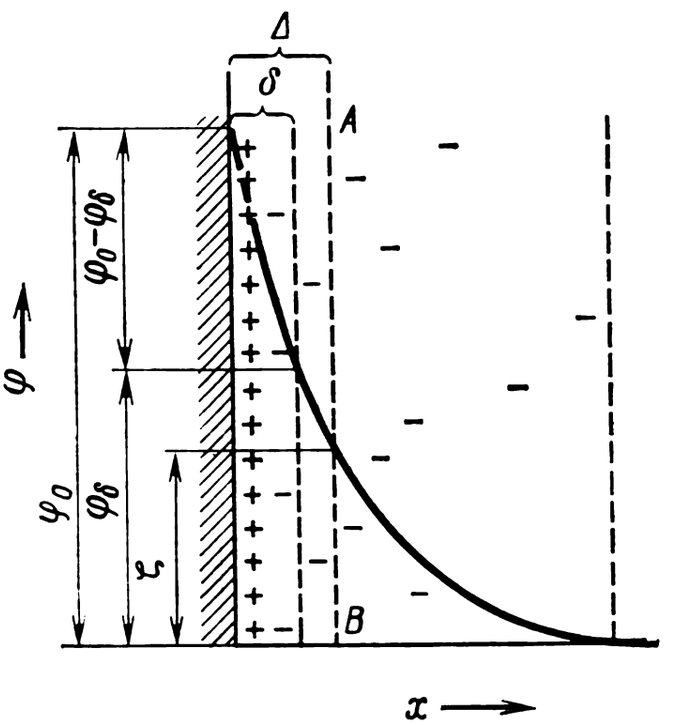

Fig. 7.11. Electric double layer according to Stern and the potential drop in it

According to Stern's theory, the distribution of ions in the electric double layer is strongly affected by the nature of counterions. If counterions have different valencies, the thickness of the diffuse layer and the number of counterions in the adsorption layer are determined mainly by the ionic valency and, consequently, depend on electrostatic forces. Of course, the diffuse layer is the thinner and the ζ-potential is the smaller, the greater is the valency of counterions. In this case, account should be taken of the same considerations as those in explaining the effect of the counterionic valency on the ζ-potential according to the Gouy-Chapman theory.

If counterions have the same valency, the thickness of the electric double layer and the number of counterions in the diffuse layer are determined by the specific adsorbability of ions, which, as we have seen in Chap. 6, depends on their polarizability α and hydration. These properties of ions are determined by their true radius or, what is the same, by the position of the elements in D. Mendeleyev's table.

The great polarizability of the ion should, of course, favour a decrease in the thickness of the electric double layer because then additional adsorption forces originate between a solid and the

induced dipole; in addition, the ion can come closer to the surface. Anions are usually polarized to a greater extent than cations because the ion deforms more as its dimensions grow and since the anionic radii are, in general, considerably greater than the cationic radii:

Cation	$\alpha \times 10^{24}$, cm^3	Anion	$\alpha \times 10^{24}$, cm^3
Li^+	0.03	F^-	0.96
Na^+	0.19	Cl^-	3.60
K^+	0.89	Br^-	5.00
Rb^+	1.50	I^-	7.60
Cs^+	2.60		

That incidentally explains why the negative surface charge is found in nature far more often than the positive one.

Ionic hydration decreases as the true ionic radius increases. A decrease in ionic hydration should promote the compression of the electric double layer because the hydrate membrane reduces electrostatic interaction between the counterions and the solid surface.

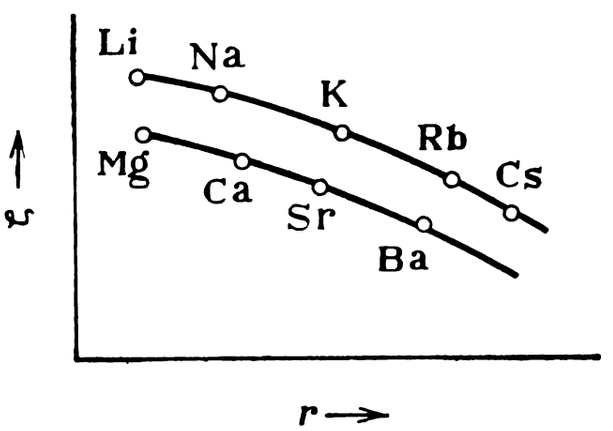

Fig. 7.12. Dependence of the ζ-potential of negatively charged clay particles on the counterion radius r

It becomes clear from the foregoing why the ability to compress the electric double layer and reduce the ζ-potential grows in the series of cations from Li^+ to Cs^+, and in the series of anions, from F^- to I^-. Fig. 7.12 shows the dependence of the ζ-potential of the negatively charged clay particles in an aqueous suspension, which is saturated with various monovalent and bivalent counterions, on the size of ions. As we may see, the dependence of the ζ-potential on the radius of bivalent cations is the same as that of monovalent cations.

Let us now consider Stern's concepts quantitatively.

According to Stern's theory, the charge σ on a solid surface is equal by its absolute value to the sum of σ_1, the charge of ions in the adsorption layer, and σ_2, the charge of the diffuse part of the double layer:

$$\sigma = \sigma_1 + \sigma_2 \qquad (7.22)$$

To calculate σ_1, Stern used the method similar to that employed for deriving the Langmuir adsorption isotherm. For a symmetrical electrolyte whose both ions bear the same value of charge, he has obtained the following equations which characterize the number of moles of ions of different signs that are adsorbed per unit area:

$$\Gamma_+ = \Gamma_{max} \frac{1}{1 + 1/c_\infty \exp\left[(\theta_+ + Fz\varphi_\delta)/RT\right]} \tag{7.23}$$

$$\Gamma_- = \Gamma_{max} \frac{1}{1 + 1/c_\infty \exp\left[(\theta_- - Fz\varphi_\delta)/RT\right]} \tag{7.24}$$

where θ_+ and θ_- are the specific adsorption potentials for positive and negative ions.

In Eqs. (7.23) and (7.24), the numerator of the exponent is the total adsorption potential of ions, i.e., the work of transfer of one mole of ions from the solution volume to the adsorbent surface. This is a complex quantity which represents the algebraic sum of the specific adsorption potential θ_+ or θ_- and the electric adsorption potential $Fz\varphi_\delta$. For positive ions, the total adsorption potential will apparently be $\theta_+ + Fz\varphi_\delta$, and for negative ions, it is $\theta_- - Fz\varphi_\delta$.

The charge σ_1 of the adsorption layer represents the difference between negative and positive charges per unit adsorption surface area. Then,

$$\sigma_1 = Fz(\Gamma_+ - \Gamma_-) = Fz\Gamma_{max} \left\{ \frac{1}{1 + 1/c_\infty \exp\left[(\theta_+ + Fz\varphi_\delta)/RT\right]} - \right.$$
$$\left. - \frac{1}{1 + 1/c_\infty \exp\left[(\theta_- - Fz\varphi_\delta)/RT\right]} \right\} \tag{7.25}$$

In practice, it is often enough to use only one of the summands in Eq. (7.25) in the calculation because either positive or negative ions are completely displaced from the molecular condenser. Another simplification consists in the discarding of unity in the denominator of both equations if the electrolytic concentration is not too high.

The charge σ_2 of the diffuse layer is directly connected with the potential φ_δ in this layer; it is calculated, according to the Gouy-Chapman theory, by Eq. (7.18), i.e., the action of adsorption forces here is not taken into account:

$$\sigma_2 = \sqrt{\frac{\varepsilon RTc_\infty}{2\pi}} \left[\exp\left(\frac{Fz\varphi_\delta}{2RT}\right) - \exp\left(-\frac{Fz\varphi_\delta}{2RT}\right) \right] \tag{7.26}$$

Substituting Eqs. (7.25) and (7.26) in Eq. (7.22), we obtain

$$\sigma = Fz\Gamma_{max} \left\{ \frac{1}{1 + 1/c_\infty \exp\left[(\theta_+ + Fz\varphi_\delta)/2RT\right]} - \right.$$
$$\left. - \frac{1}{1 + 1/c_\infty \exp\left[(\theta_- - Fz\varphi_\delta)/2RT\right]} \right\} +$$
$$+ \sqrt{\frac{\varepsilon RTc_\infty}{2\pi}} \left[\exp\left(\frac{Fz\varphi_\delta}{2RT}\right) - \exp\left(-\frac{Fz\varphi_\delta}{2RT}\right) \right] \tag{7.27}$$

The value of the first term of the expression in braces in the right-hand member of the equation changes with concentration to a greater extent than that of the second one; then, apparently, when the solution is diluted, σ_1 changes more rapidly than σ_2 and the structure of the double layer approximates the Gouy-Chapman model; when the concentration increases, the structure of the double layer approximates the Helmholtz model. Hence, the analysis of Eq. (7.27) leads to the same conclusions as those we have drawn earlier on the basis of general principles.

The first term of the sum in the right-hand member of the equation, σ_1, is of interest also because even when θ_+ and θ_- are equal to zero, i.e., when specific adsorption is absent, the quantity σ_1 is not equal to zero. This means that even if counterions are not adsorbed specifically, they can be drawn into the adsorption layer by electrostatic forces.

C, the total capacity of a double layer, is defined as the capacity of two consecutively arranged condensers according to the formula

$$C = \frac{C_m \cdot C_d}{C_m + C_d} \tag{7.28}$$

where C_m = capacity of the molecular condenser;
C_d = capacity of the diffuse layer.

C_m, the capacity of the molecular layer, is equal to the ratio of σ, the charge of the wall, to the difference in potentials $(\varphi_0 - \varphi_\delta)$:

$$C_m = \sigma/(\varphi_0 - \varphi_\delta) \tag{7.29}$$

Stern took the capacity of the molecular condenser as constant. However, this capacity should depend on the specific properties of ions which are in the adsorption layer. Since C_m is almost constant and C_d greatly depends on the concentration of an electrolyte, the drop of the potential in the electric double layer also depends on the concentration of the electrolyte in a system. Hence, even if the potential φ_0 is constant, φ_δ whose value is determined by the state of the diffuse layer decreases with $1/\varkappa$.

If the capacity of one of the two condensers is considerably greater than that of the other, the total capacity, for all practical purposes, is equal to the smaller constituent. Hence, in dilute solutions, $C \approx \approx C_d$, while in concentrated ones, $C \approx C_m$.

The values of the capacity of the electric double layer, calculated according to the Stern theory with regard to ionic radii, are similar to the empirical values, and therefore the theory overcame one of the shortcomings of the Gouy-Chapman theory. In addition, unlike the Gouy-Chapman theory, the Stern theory can explain why the sign of the electrokinetic potential changes when polyvalent ions whose charge is opposite in sign to that of the dispersed phase are intro-

duced into a system. Such polyvalent ions enter the adsorption layer owing to both strong electrostatic interactions and great adsorbability connected with the polarizability of such ions. Ions can be adsorbed in so great an amount that they not only neutralize the charge of the solid surface, but also reverse its charge. Then, as may be seen from Fig. 7.13, the pattern of the potential drop in the electric double layer changes whereas the φ_δ- and ζ-potentials which earlier had the same sign as the φ-potential ($\varphi_{\delta 1}$ and ζ_1 in the scheme) change to the opposite sign ($\varphi_{\delta 2}$ and ζ_2 in the scheme). Of course in this case, the potential φ_0 remains constant because extraneous ions are incapable of completing the construction of the crystal lattice of a solid. Hence, φ_0- and ζ-potentials have different signs. Of course, a further increase in the concentration of an electrolyte in a system should cause the diffuse layer to contract and the ζ-potential to drop.

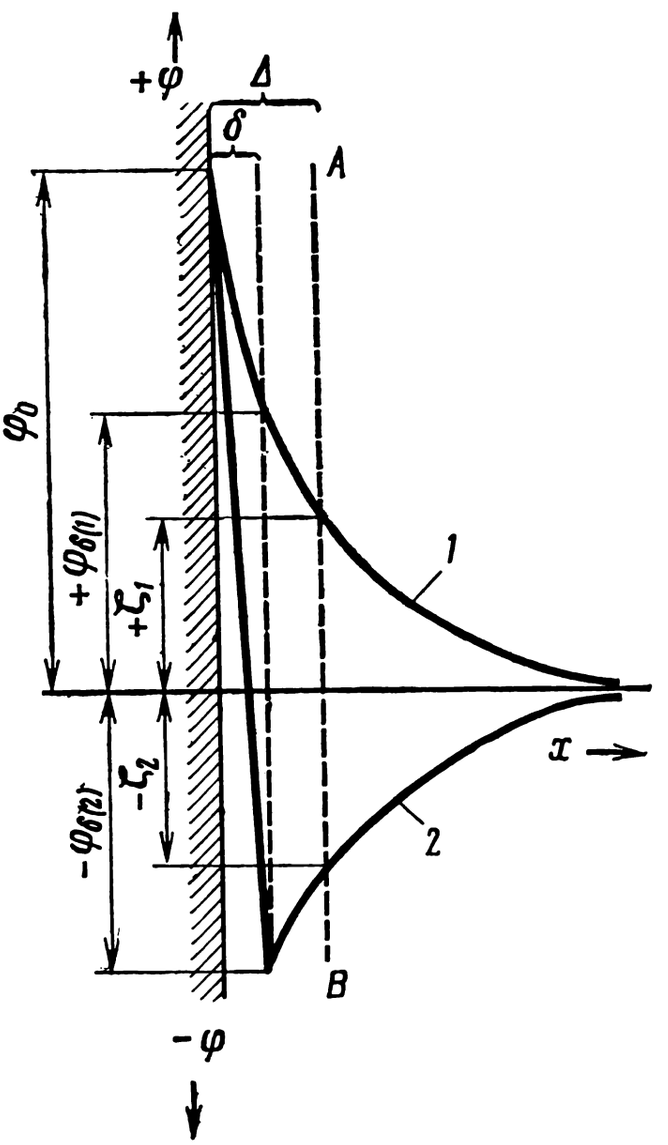

Fig. 7.13. Potential drop in the electric double layer changed after a recharge by strongly adsorbed ions: *1*—potential drop before a recharge; *2*—potential drop after a recharge

Polyvalent ions of aluminium and thorium are often used for recharging the particles which have a negative ζ-potential. In fact, monovalent ions can also cause a recharge if they have a great adsorption potential. There are ions of many alkaloids, such as strychnine and quinine, and basic dyes such as crystal violet and methylene blue. This is because such large ions not only can be polarized, but also have constant dipole moments.

It follows from the foregoing that the Stern theory corresponds to experimental results better than the Gouy-Chapman theory. Since it specifies the role of the ion dimensions and introduces the concept of the adsorption potential, it can explain several features of the action of electrolytes on the electric double layer and the electrokinetic potential. However, this theory is also not perfect because it is based on several assumptions and has many ambiguities, e.g., it allows the adsorption potential to be independent of concentration, which

is hardly probable. The concepts of the slipping plane in the electric double layer are not accurate. The slipping plane as conceived by Stern apparently does not exist: there is the slippage of liquid from the interface deep into the solution, and it begins at a certain distance from the solid surface. Thus, the value of the ζ-potential, an important characteristic of any colloidal system, is determined in electrokinetic phenomena not only by the nature of the potential drop in the electric double layer, but also by the nature of liquid motion near the solid surface that depends on its rheological properties.

Several studies were later carried out in order to specify Stern's assumed structure of the electric double layer. Among them, of the greatest importance is Graham's work according to which the Helmholtz layer consists of external and internal parts. The external part contains hydrated counterions which are retained at the interface by electrostatic forces. The internal part contains ions which are chemisorbed by the solid surface, carry a charge of the same sign as that of the solid and have partially destroyed hydrate shells.

Structure of the electric double layer of spherical particles. For spherical particles at comparatively small values of the potential φ_0, the approximate expression of the potential drop with distance was given by Debye and Hückel:

$$\varphi = (\varphi_0 r/a) \exp [-\varkappa (a - r)] \qquad (7.30)$$

where r is the radius of the particle, and a, the distance from its centre.

The particle charge Q in this case depends on the potential φ_0 in the following way:

$$Q = r\varepsilon (1 + \varkappa r) \varphi_0 \qquad (7.31)$$

It is still very hard to find such relations for high values of the potential φ_0 owing to fundamental and mathematical difficulties that arise in this case. However, there are special tables compiled by Loeb, Oberbeek and Wiersema that make it possible to find the connection between the charge and the potential of spherical particles.

Structure of the electric double layer of particles having a constant dipole moment. N. Tolstoi and his coworkers have shown that there are colloidal particles with an electric dipole structure which are formed as a result of the spontaneous unipolar orientation of dipoles of the dispersion medium (e.g., H_2O, OH^-) that are adsorbed on their surface, or of the orientation of polar groups of the substance of particles. As various electro-optical methods of investigation have shown, such particles have a large, fixed electric moment (thousands and millions of Debye units). For example, a permanent dipole structure has been discovered in vanadium pentoxide, particles of

clay suspensions, humus sols, the suspensions of several dyes, and some bacteria and viruses. Such dipole structures which have recently drawn the attention of scientists are widespread in colloidal and biological systems.

Owing to the presence of constant dipoles, particles can interact with one another and form complex structures in a sol.

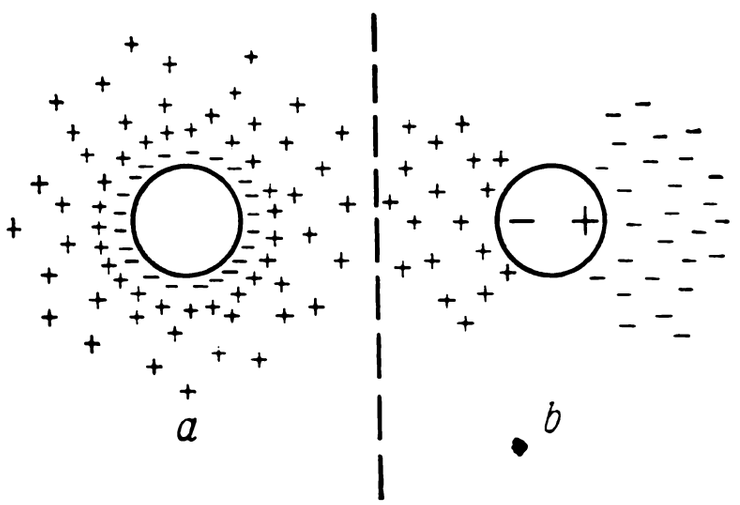

Fig. 7.14. Diagram of the structure of the ionic double layer of ordinary and dipole colloidal particles (according to I. Yefremov):
a—ordinary colloidal particle; *b*—dipole colloidal particle

The electric structure of a colloidal particle which has a constant dipole can, as the first approximation, be represented as the interaction between the electric double layer of Gouy-Chapman and the dipole structure (Fig. 7.14).

Similar interactions are observed also in magnetic dispersed particles.

3. EFFECT OF DIFFERENT FACTORS ON THE ELECTROKINETIC POTENTIAL

Since, in some cases, the ζ-potential is a quantity which characterizes the stability of a colloidal system, one should consider the effect on it of such factors as the introduction of electrolytes into a system, a change in pH, in the concentration of a solution, in temperature, and so forth.

Effect of indifferent electrolytes. It is expedient to begin the consideration of the effect of various factors on the ζ-potential with the simplest and important practical case: the introduction into a system of indifferent electrolytes, i.e., electrolytes which do not have ions capable of completing the construction of the crystal lattice of a colloidal particle. In practice, it is precisely indifferent electrolytes that are most often introduced in order to coagulate colloidal systems.

Indifferent electrolytes cannot substantially change the total jump in the potential of colloidal particles; in general, they decrease the electrokinetic potential by increasing the concentration of counterions and contracting the electric double layer.

With indifferent electrolytes, two cases should be distinguished: (1) an electrolyte, one of whose ions is the same as counterions, is introduced into a system; (2) an electrolyte which does not have common ions with the stabilizer electrolyte is introduced into a system.

The first case was considered when we discussed the Gouy-Chapman and Stern theories. Apparently, as the content of such an electrolyte increases in a system, the thickness of the electric double layer tends to become equal to that of the adsorption layer owing to the contraction of the diffuse layer. As a result, the ζ-potential decreases until it becomes zero, and this will correspond to the *isoelectric state of a system.*

The second case when an electrolyte which does not have either of the ions of the stabilizer electrolyte is introduced differs from the first only in that the counterions of a colloidal particle are exchanged for an equivalent number of ions of the electrolyte introduced that bear the charge of the same sign. The simplest exchange of ions occurs when such an electric double layer as the Gouy-Chapman one is on the solid surface, i.e., when the specific adsorption potential of ions can be neglected. Apparently, in this case, exchange will be determined only by ionic valency. For example, if a negatively charged dispersed phase is in a solution which contains two types of monovalent cations, the ratio between the concentrations of these ions at any point of the double layer should be the same as that in the bulk of the solution. Ion exchange will apparently follow the ratio which is similar to B. Nikolsky's equation (6.6)

$$g_1/g_2 = c_1/c_2 \qquad (7.32)$$

where g_1 and g_2 = concentration of ions *1* and *2* of an electrolyte in the double layer;
c_1 and c_2 = concentration of these ions in the solution.

If the valency of counterions is not the same, the equilibrium in exchange is shifted towards the cation of a higher valency which accumulates in a greater quantity in places having a negative potential.

Ion exchange is complicated when there is specific ion adsorption. In this case, ions of the same valency are arranged, according to their ability to pass over to the electric double layer, in the same series as those which were given when the dependence of the thickness of the electric double layer on the nature of the ions forming it was discussed.

Many equations that quantitatively describe ion exchange and take account of specific ion adsorption have been proposed. The most general of these which can be applied only to the exchange of ions of the same valency is

$$g_1/g_2 = f\,(c_1/c_2) \tag{7.33}$$

The coefficient f is a quantity which depends on the difference in the specific adsorption potentials θ_1 and θ_2 of both ions:

$$f = \exp\left[\frac{\theta_1 - \theta_2}{RT}\right] \tag{7.34}$$

When the adsorption potential is very high, ions whose charge is opposite in sign to that of the dispersed phase can cause the reversal of charge of colloidal particles. This phenomenon was considered when the Stern theory was expounded.

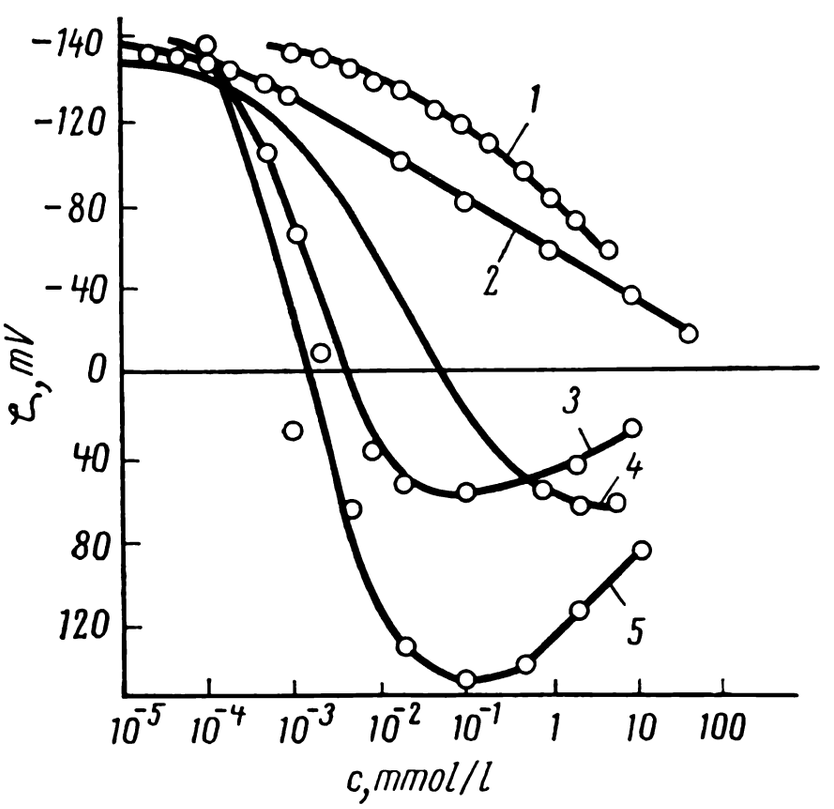

Fig. 7.15. Effect of electrolytes on the ζ-potential of the glass interface: *1*—KCl; *2*—$Ca(NO_3)_2$; *3*—$Al(NO_3)_3$; *4*—methyl violet; *5*—$Th(NO_3)_4$

Fig. 7.15 shows, as an example, curves plotted by A. Rutgers and M. De Smet to characterize the change in the ζ-potential of glass when different electrolytes are introduced into a colloidal solution. The negative values of the ζ-potential are plotted on the ordinate above zero, and its positive values, below zero. Such a graphic presentation is often used in colloid chemistry because particles are charged negatively in most colloidal systems. As we may see, electrolytes having monovalent and bivalent cations (curves *1*, *2*) only

reduce the ζ-potential of the negatively charged glass surface whereas those having trivalent and tetravalent cations cause a reversal of charge (curves *3*, *4*, *5*).

In considering the effect of indifferent electrolytes, we assumed that the electrokinetic potential is affected by ions whose charge is opposite in sign to that of the colloidal particle, and is the same as the charge of counterions. But can the ζ-potential be affected by accompanying or co-ions of an indifferent electrolyte that bear a charge of the same sign as the colloidal particle? The answers to this question are different but, even if these ions do affect the electrokinetic potential, it is only to an inconsiderable extent. We shall discuss this again in Chap. 9.

Effect of non-indifferent electrolytes. Ions of such electrolytes are capable of completing the construction of the crystal lattice of

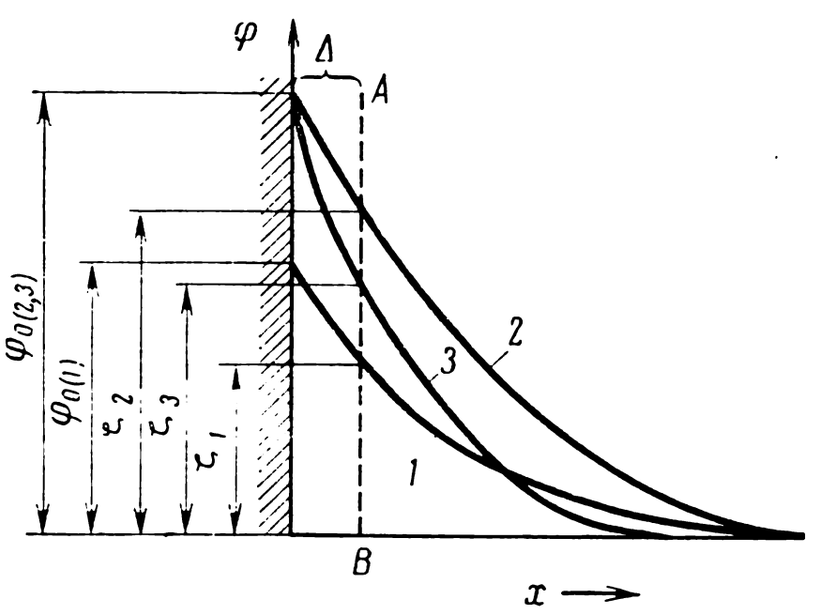

Fig. 7.16. Effect of a non-indifferent electrolyte on the φ_0-potential and ζ-potential:

1—the potential drop in the electric double layer before the introduction of an electrolyte; *2*—the same after the introduction of a non-indifferent electrolyte; *3*—the same after the addition of a considerable amount of a non-indifferent electrolyte

a dispersed phase. The potential-determining ion of the electrolyte can raise the potential φ_0 whereas the remaining ion whose charge is of the same sign as that of the counterion can compress the electric double layer. The first tendency, connected with the surface action of the ion that is capable of completing the construction of the crystal lattice, is mainly exhibited at low concentrations of a non-indifferent electrolyte. The second tendency prevails at high concentrations when the construction of the crystal lattice is completed. Therefore, when an increasing amount of a non-indifferent electrolyte is introduced into a system, the ζ-potential first grows, reaching the maximum, and then drops. This is schematically illustrated in Fig. 7.16.

Fig. 7.17 shows the change in the φ_0- and ζ-potentials of particles of a silver iodide sol as a function of the logarithm of concentration of iodide ions (log c_{I^-}) in a solution (the data of S. Troelstra and H. Kruyt). The pattern of the change in both potentials with the concentration of potential-determining ions confirms the foregoing.

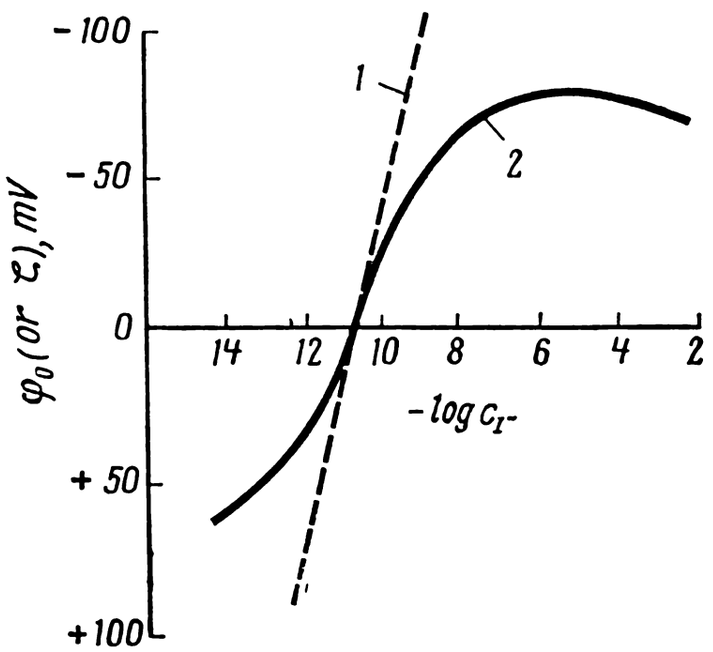

Fig. 7.17. Dependence of the φ_0-potential (curve *1*) and the ζ-potential (curve *2*) of the **AgI** sol particles on the logarithm of the concentration of iodide ions in a solution

When a non-indifferent electrolyte is introduced, the charge of colloidal particles may also be reversed, as can be seen from the example. A potassium iodide solution is added to a sol of silver iodide which is stabilized by silver nitrate. Before the electrolyte is introduced, the potential-determining ion in the sol is Ag^+, and the counterion, NO_3^-. The particles of such a sol are charged positively. After an excess of potassium iodide is introduced into a system, the potential-determining ion will be I^-, and the counterion, K^+. Sol particles will become negatively charged. In addition, silver nitrate which is contained in the dispersion medium will react with potassium iodide; as a result, an additional amount of the negatively charged dispersed phase appears in the system. This charge reversal differs from that produced by extraneous ions in that not only the ζ-potential, but also the φ_0-potential, change. The charge reversal of the dispersed phase by a non-indifferent electrolyte is schematically illustrated in Fig. 7.18.

Effect of the pH of the medium. The pH value of the dispersion medium can strongly affect the ζ-potential of colloidal particles, because hydrogen and hydroxyl ions have great adsorbability; this is true of the former because their small radius allows them to

approach the solid surface closely, and likewise of the latter because of their great dipole moment.

The pH effect is especially important to lyosols whose dispersed phase is an amphoteric compound, such as the sols $Al(OH)_3$, $Fe(OH)_3$, $Sn(OH)_4$ and $Th(OH)_4$. As the pH of the dispersion medium changes, the charge of these sols may be reversed owing to a change in the nature of ionization of the substance of the dispersed phase. Let us consider such a reversal of charge by taking the example of the sol of aluminium hydroxide.

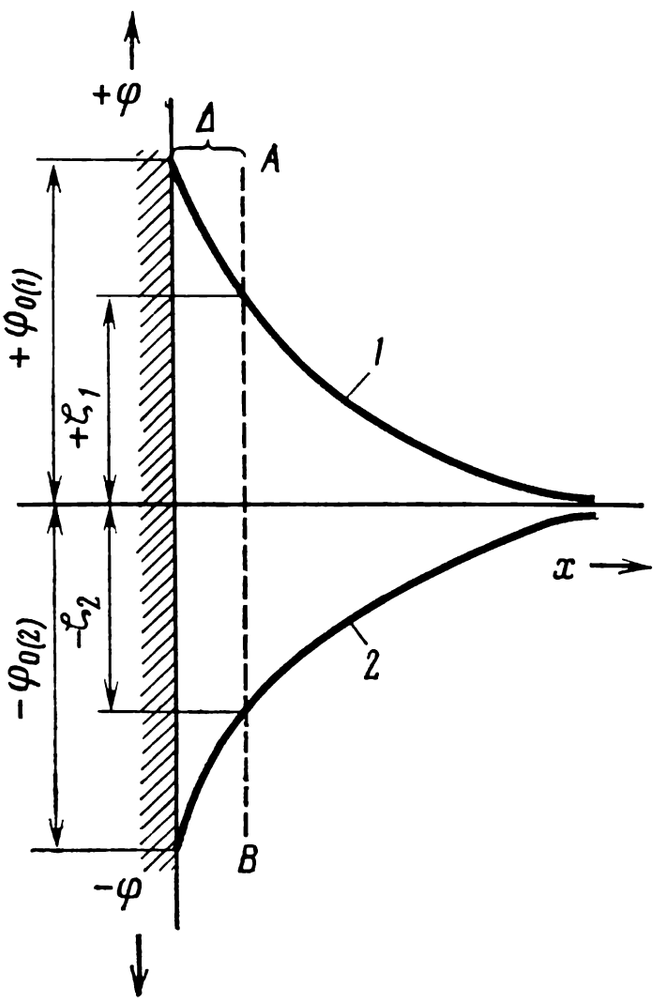

Fig. 7.18. Drop of the φ_0-potential and ζ-potential changed after a recharge by a non-indifferent electrolyte: *1*—potential drop before a recharge; *2*—potential drop after a recharge

When the medium is not too acidic, the $Al(OH)_3$ molecules on the surface of colloidal particles are ionized in the following way:

$$Al(OH)_3 \rightleftarrows Al(OH)_2^+ + OH^-$$

Hydroxide acts as a base because an excess of hydrogen ions suppresses acid ionization. As a result, the potential-determining ion is $Al(OH)_2^+$, and the counterion is OH^-. The colloidal particle is charged positively.

In media having a lower pH, the ions Al^{3+} are formed:

$$Al(OH)_2^+ + OH^- \rightleftarrows Al^{3+} + 3OH^-$$

At first, this causes an increase in the total positive charge of the surface, then aluminium hydroxide dissolves in acid, and, consequently, the colloidal solution becomes a true one.

In the alkaline medium, basic ionization cannot occur owing to the excess of hydroxyl ions. In this medium, aluminium hydroxide acts as an acid, and $Al(OH)_3$ is ionized:

$$Al(OH)_3 \rightleftarrows Al(OH)_2O^- + H^+$$

As a result, the potential-determining ion is $Al(OH)_2O^-$, and the counterion, H^+. The colloidal particle is charged negatively.

In media having a higher pH, the ion AlO_2^- is formed:

$$Al(OH)_2O^- + H^+ \rightleftarrows AlO_2^- + H^+ + H_2O$$

When the concentration of hydroxyl ions is even higher, aluminium hydroxide dissolves in the alkaline solution yielding aluminate, and the colloidal solution becomes a true one.

Of course, if the φ_0-potential changes, the ζ-potential of colloidal particles will also change. In the acid medium, the ζ-potential, like the φ_0-potential, has a positive sign, and in the alkaline medium, a negative one. There should be a pH value at which the ζ-potential is equal to zero and the system is in the isoelectric state when there is an equal number of positive and negative charges on the surface.

The given example of charge reversal of the dispersed phase differs from the previously considered change in the sign of the ζ-potential when a non-indifferent electrolyte is added only in that the ion, which determines the potential after the reversal of charge, is not added to a system, but is formed out of the substance of the dispersed phase as a result of a change in the nature of ionization.

Effect of the concentration of a colloidal system. It may be generally assumed that the ζ-potential should grow when any colloidal system is diluted because the thickness of the electric double layer increases with a decrease in the concentration of counterions in a solution. At the same time, the potential-determining ion may be desorbed from the surface of the dispersed phase during dilution, and this should cause the φ_0-potential and the ζ-potential to drop. The concentration of a colloidal system, of course, causes a directly opposite action. The direction in which the ζ-potential ultimately changes when the concentration of the colloidal system alters is apparently determined by the fact which of the two factors, i.e., the thickening (contraction) of the electric double layer or the desorption (adsorption) of potential-determining ions, produces a stronger effect.

Effect of temperature. Temperature acts similarly as concentration on the ζ-potential. As temperature rises, the ζ-potential should grow owing to the intensification of the thermal motion of counterions and an increase in the thickness of the electric double layer. However, the desorption of potential-determining ions may also grow simultaneously, and then the φ_0- and ζ-potentials decrease. There should be an inverse relationship when temperature drops. The problem of how the ζ-potential will be altered with a change in temperature should apparently be solved separately for every colloidal system.

Of course, the foregoing considerations are valid only when the dilution (heating) or concentration (cooling) of a system does not considerably affect both the solubility of a stabilizing electrolyte and its conversion from a molecular to an ionized form.

Unfortunately, there are very little experimental data on the effect of both the concentration of the dispersed phase and temperature on the ζ-potential of particles of various lyosols.

Effect of the nature of the dispersion medium. As we have seen at the beginning of this chapter, electrokinetic phenomena and, consequently, the presence of the electric double layer at the interface are characteristic of systems having polar dispersion media. The ζ-potential of the dispersed phase is the larger, the greater is the polarity of the solvent. Table 7.1 presents the rates of electroosmotic transfer of some pure liquids in glass capillaries that have been obtained in experiments carried out by Fairbrother and Balkin. One can see that the greater the polarity of a liquid, characterized by its dielectric constant and the dipole moment of a molecule, the higher is the rate of electroosmotic transfer.

Table 7.1. **Rates of Electroosmotic Transfer of Various Liquids in Glass Capillaries**

Liquid	Dielectric constant	Dipole moment of a molecule $\mu \cdot 10^{18}$, electrostatic units	Rate of electroosmotic transfer $u_0 \cdot 10^5$, $cm^2/sec \cdot V$
Water	81	1.85	16.16
Nitrobenzene	36	3.9	5.53
Propyl alcohol	22	1.75	1.95
Aniline	7.2	1.51	1.15
Chloroform	5.2	1.06	0.63
Benzene	2.25	0	0
Carbon tetrachloride	2.23	0	0

Effect of non-equilibrium electric surface forces. Earlier we considered the equilibrium surface forces that operate at the interface and can prevent two particles of like charge from drawing together. Recently, B. Deryagin and S. Dukhin analysed the action of electric surface forces in systems whose thermodynamic equilibrium is upset. They established that the deformation of the electric double layer, caused by the external electric field or by the convective motion of a liquid, can lead to the formation of an electric field whose radius of action is often several orders larger than that of the undeformed layer under the same conditions.

The polarization of the electric double layer has also been treated by Oberbeek, Booth, Newman, and other authors who concluded that the osmotic effect can be neglected when the value of the ζ-potential is low ($\zeta < 25$ mV) or the electric double layer is very thin.

The theory of non-equilibrium surface forces of a diffusive nature, evolved by Deryagin and Dukhin, is important when the electrokinetic phenomena and the interaction of polarized particles are being considered. By taking account of the diffusion and polarization of

the double layer, Deryagin and Dukhin predicted a new phenomenon related to electrophoresis, i.e., *diffusio-phoresis*, consisting in the movement of dispersed particles, when the external electric field is absent, under the action of a gradient of ion concentration.

The electric surface, non-equilibrium forces can play an important role in various processes. The electric double layer can be deformed not only by the external electric field (this will be considered in Sec. 5 of this chapter), but also by convective flows of the liquid medium, the gravitational field, the centrifugal force field, the ultrasound field, mechanical vibrations, and Brownian motion. In particular, the electric field, which originates when fine particles settle, affects the sedimentation rate. It was indicated by V. Levich and A. Frumkin that an electric field of a diffusive origin may appear near the surface of a drop that moves in the liquid medium. The polarization of ionic layers, caused by the deformation of the double layer, brings about the appearance of the long-range forces of attraction between induced dipoles. J. Stauff observed the formation of periodic structures from non-conducting colloidal particles that are in the variable electric field. Some of these effects are considered in greater detail in Chap. 9.

4. ELECTROPHORESIS AND ELECTROOSMOSIS

The phenomena of electrophoresis and electroosmosis have been described in the most general form at the beginning of this chapter. Let us consider the elementary theory of electrokinetic phenomena and the methods of determining electrophoretic mobility and the rate of electroosmotic transfer in greater detail because these quantities make it possible to calculate an important characteristic of colloidal systems, i.e., the ζ-potential.

According to G. Quincke, electrokinetic phenomena are caused by the electric double layer that originates at the interface. H. Helmholtz evolved Quincke's ideas and tried to interpret these phenomena quantitatively, based on the following principles.

1. The electric charges of the surfaces of a liquid and of a solid are opposite in sign and parallel to one another, as a result of which the electric double layer is formed.

2. The thickness of the electric double layer has dimensions similar to molecular ones.

3. In electrokinetic phenomena, the layer of liquid immediately bordering on the solid surface remains stationary; the remaining liquid, being near this surface, moves and obeys the friction law which is applied to ordinary liquids.

4. The flow of liquid in the electric double layer during electrokinetic phenomena is laminar and is expressed by ordinary hydrodynamic equations.

5. The electric double layer can be regarded as a parallel-plate condenser.

6. The distribution of charges in the double layer does not depend on the voltage of the electric field, and the outer difference in potentials is simply added to the field of the electric double layer.

7. The solid is a dielectric, and the liquid conducts electric current.

Let us use these principles to derive an equation that connects the ζ-potential with the rate of electrophoresis or electroosmotic transfer. To this end, let us suppose that the solid surface has an electric

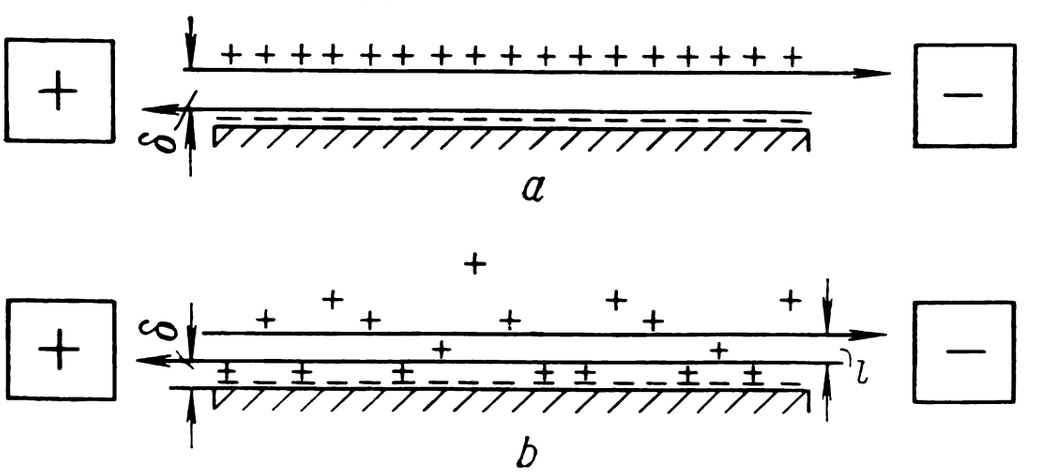

Fig. 7.19. Behaviour of the electric double layer in electrokinetic phenomena: *a*—diagram of the double layer according to Helmholtz and Perrin; *b*—diagram of the double layer (Gouy's diffuse layer and Stern's adsorption layer)

double layer which is under the action of the difference in electric potentials that is tangential to the inferface (Fig. 7.19*a*). The ions (counterions) which are in the liquid tend, under the action of the external electric field, to move to the right towards the pole which carries an opposite charge (in this case, towards the cathode). Of course, near the solid surface, the liquid also tends to move with the ions. Under the action of the same field, the solid surface with the potential-determining ions attached to it tends to move in the opposite direction (in this case, towards the anode). The movement of a solid (electrophoresis) or of a liquid (electroosmosis) depends on whether the liquid or the solid surface is stationary.

If we displace one phase relative to another, instead of applying the potential difference to the electric double layer, electric charges which are connected with the phase will be transferred, yielding an electric current, and, consequently, the potential difference. Either the streaming potential or the Dorn potential, depending on whether the liquid moves relative to the stationary solid wall or solid particles move in the liquid, will be observed.

Suppose that the distance between potential-determining ions which are connected with a solid and ions which are in a liquid is equal to δ and that the quantity of the elementary electric charge multi-

plied by the number of unit electric charges per unit surface area of the solid (surface density) is equal to σ. Since the system is electroneutral, the surface density of a charge in the liquid should also be equal to σ, but with the opposite sign. This condensation of electric energy near the interface is equivalent to the condenser charge and corresponds to the difference in potentials ζ between its plates or, accordingly, between phases. Since δ is a very small quantity, the curvature of the interface can be neglected, thus considering the electric double layer to be a plane condenser. There is the following relationship between the quantities δ, σ and ζ for a plane parallel-plate condenser:

$$\zeta = 4\pi\delta\sigma/\varepsilon \tag{7.35}$$

where ε is the dielectric constant of a substance between the condenser plates.

That same equation can be rewritten as

$$\sigma = \varepsilon\zeta/(4\pi\delta) \tag{7.36}$$

If the potential difference E is applied tangentially to the double electric layer of ions, and the distance between electrodes is L, the potential gradient H of the external field will be

$$H = E/L \tag{7.37}$$

The electric force acting tangentially per unit interface area, when the latter is in the electric field which has the potential gradient H, and tending to shift two phases relative to one another is

$$F_1 = \sigma H \tag{7.38}$$

Both electrophoresis and electroosmosis occur at a constant rate after a short lapse of time during which steady state is established, only because the friction force counterbalances the electric force that causes the displacement of phases. According to Newton's law, the friction force per unit interface area is

$$F_2 = \eta\,(du/dl) \tag{7.39}$$

where η = dynamic viscosity of a liquid;
u = rate of movement of the liquid relative to the solid wall;
l = thickness of the layer of a liquid in which its rate of movement changes; it is equal to the distance between the condenser plates δ according to the scheme of the electric double layer.

Assuming that the flow rate of a liquid in the electric double layer changes linearly with distance and taking into account that $l = \delta$ we obtain

$$F_2 = \eta\,(u/\delta) \tag{7.40}$$

Since, at a constant rate of electrophoresis or electroosmosis, the electric force which causes motion and the friction force are equal, i.e., $F_1 = F_2$, then

$$\sigma H = \eta\,(u/\delta) \tag{7.41}$$

Substituting the value of σ taken from Eq. (7.36) in Eq. (7.41), performing the necessary cancellations, and solving it relative to u, we obtain the Helmholtz-Smoluchowski equation

$$u = \varepsilon\zeta H/(4\pi\eta) \tag{7.42}$$

The rate of electrophoretic transfer is very often referred to unit gradient of the potential applied, and for this purpose both members of Eq. (7.42) are divided by H:

$$u_0 = u/H = \varepsilon\zeta/(4\pi\eta) \tag{7.43}$$

The quantity u_0 is known as *electrophoretic mobility* and is used for comparing the electrophoretic ability of various colloidal systems.

Solving Eq. (7.42) in respect to the ζ-potential, we obtain

$$\zeta = 4\pi\eta u/(\varepsilon H) \tag{7.44}$$

Using Eq. (7.44), we can calculate the ζ-potential in electrophoresis or electroosmosis if the quantity u is known. It should be borne in mind that, if the applied potential difference E is expressed in V, and L in cm, then $H = E/L$ (V/cm) $= E/L \cdot 300$ (electrostatic units per centimetre). The potential expressed in absolute electrostatic units can be found by the equation

$$\zeta = 4\pi\eta u/(\varepsilon H) = 4\pi\eta u L \cdot 300/(\varepsilon E) \tag{7.45}$$

However, the ζ-potential, like any other electrostatic potential, is expressed in volts. To this end, the value of the potential calculated by Eq. (7.45) must be multiplied again by 300. The equation for calculating the electrokinetic potential in volts is

$$\zeta = 4\pi\eta u L \cdot 300^2/(\varepsilon E) \tag{7.46}$$

When Eqs. (7.42) and (7.44) were derived, several simplifications and not fully substantiated assumptions were made. To begin with, the scheme of the structure of the electric double layer is not satisfactory. According to the latest concepts, the electric double layer should be regarded not as a plane parallel-plate condenser, but as a condenser one of whose plates consists of diffused ions. A part of these ions is in the layer near the surface and is away from the solid surface at a smaller distance than the slipping plane. As a result, the electrokinetic potential corresponds not to the entire charge on the wall surface, but to the difference between the total surface charge and the charge of all the counterions in the layer near the surface. The behaviour of such a layer in electrophoresis or electro-

osmosis is schematically represented in Fig. 7.19*b*. True, such a concept of the electric double layer does not underrate the given conclusion since this layer can still be regarded as an electric condenser. The only question that arises is whether distance l, at which the rate of a liquid flow in the double layer changes, can be equated in calculations to the average distance between both plates of an electric condenser having a diffused external plate.

Furthermore, since slippage occurs not on a plane, but in a layer which has a small, yet a finite thickness and contains a certain number of counterions, changes in the rate of a liquid flow in this layer with distance do not strictly obey the linear law. Hence, the allowance that $du/dl = u/l$ is somewhat nominal.

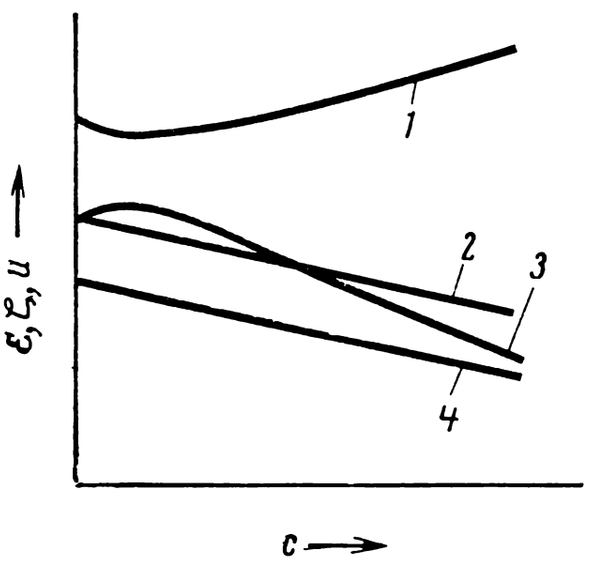

Fig. 7.20. Effect of concentration c of an electrolyte in a solution on the electrokinetic properties of a system: *1*—change in the dielectric constant ε; *2*—change in the ζ-potential which is calculated without taking account of the change in ε; *3*—change in the ζ-potential which is calculated with regard to the change in ε; *4*—change in electrophoretic mobility u

Lastly, by assuming the values of the dielectric constant and of the coefficient of viscosity of a liquid in the electric double layer to be equal to their values in a solution, we also make a certain error because the values of ε and η in the electric double layer can be other than those in the dispersion medium owing to the high concentration of ions. The dielectric constant can also be affected by the field of high voltage in the electric double layer. Viscosity at the solid surface may increase due to a change in the structure of the liquid layer near the surface which is caused by molecular forces, as was indicated by Deryagin. In addition, both the dielectric constant and viscosity are macroconstants and, strictly speaking, cannot be used in calculating the ζ-potential when they should characterize a liquid layer of molecular thickness.

The difference between the values of the dielectric constant and viscosity in the electric double layer, on the one hand, and the values of these characteristics in the volume of the dispersion medium, on the other, not only gives incorrect absolute values of the ζ-potential, but also changes the effect of various factors on the ζ-potential. To illustrate this principle, let us take the following example. We know that when the electrolyte concentration grows, the dielectric constant of the solution changes, passing through the minimum. As a result, the ζ-potential, calculated by the Helmholtz-

Smoluchowski equation with regard to a change in ε, will change along the curve with the maximum even if electrophoretic mobility changes with an increase in the electrolyte concentration according to the linear law. The foregoing is illustrated in Fig. 7.20.

In determining the values of the ζ-potential by electrophoresis and electroosmosis, one comes across experimental and theoretical difficulties which we will deal with below. Nevertheless, one should not conclude that the empirical quantities of the ζ-potential are quite erroneous. All experimental evidence indicates that even if the absolute value of the electrokinetic potential is determined not quite accurately, a correct general picture of its changes under the action of various factors can still be obtained.

5. DETERMINATION OF THE ELECTROKINETIC POTENTIAL

Electrophoretic methods. The value of the ζ-potential can be calculated by Eq. (7.44). For this purpose, it is necessary to measure the rate of the electrophoretic movement of particles in a system at a given potential gradient of the voltage applied, and to know the values of viscosity and of the dielectric constant of a liquid.

However, before considering the experimental methods of determining the rate of electrophoretic transfer, let us deal with various types of limitations which should be taken into account when Eqs. (7.42) and (7.44) are used.

According to the basic principles, electrophoresis is similar to electroosmosis. For both electrophoresis and electroosmosis, the movement of a liquid relative to the surface of a solid is determined by forces acting on the electric double layer. It is precisely on the basis of these assumptions that the Helmholtz-Smoluchowski equation is derived, which expresses the dependence of the rate of electrophoresis on the potential gradient of the external electric field. However, the use of Eq. (7.42) for electrophoresis is limited by the following requirements. First of all, the thickness of the double layer (which is usually characterized by the quantity $1/\varkappa$) should be small in comparison with the particle dimensions. Secondly, the substance of a particle should not conduct electricity, and surface conductivity at the interface should be so small that it would hardly affect the distribution of the external electric field.

The Helmholtz-Smoluchowski equation was long held to be valid for all cases, regardless of whether the foregoing requirements were met or not. But in 1924, Hückel, on the basis of a new theory of strong electrolytes, gave another equation which differed from Eq. (7.42) by the numerical factor 2/3:

$$u = \varepsilon\zeta H/(6\pi\eta) \qquad (7.47)$$

In deriving this equation, the colloidal particle is taken as being equivalent to a spherical one, and a correction is introduced for *electrophoretic retardation* which is caused by the effect of the external field on the electric double layer. Under the action of this field, counterions move in the direction opposite to the movement of the particle, thus making the surrounding liquid to move in the same direction. This causes a particle to move not in a liquid which is at rest, but in a liquid which is in motion, as a result of which the electrophoretic rate decreases.

Henry showed in 1931 that both Eqs. (7.42) and (7.47) were valid each in an individual case. In deriving Eq. (7.42), account was taken of the deformation of the electric field caused by a non-conducting particle, and in deriving Eq. (7.47), it was assumed that non-conducting particles did not affect the field in the double layer and in the liquid volume. The latter assumption is valid only when the electric conductivity of particles is equal to that of the medium or when the particle dimensions are so small in comparison with the thickness of the double layer that deformation in the greater part of the double layer is inconsiderable.

Carefully considering the question from the mathematical viewpoint and taking account of the deformation of the external field, Henry showed that the rate of electrophoresis can, in all cases, be expressed by the equation

$$u = f\varepsilon\zeta H/(\pi\eta) \tag{7.48}$$

where f = function of the quantity $\varkappa a$;
a = radius of a spherical or a long cylindrical particle;
$\varkappa$ = reciprocal of the thickness of the double layer.

The value of the quantity f depends on the shape of particles and their orientation in the field. The dependence of this quantity on $\varkappa a$ is shown in Fig. 7.21.

For non-conducting cylindrical particles whose axis is in the same direction as the field, $f = 1/4$, as in Eq. (7.42). For cylindrical particles which are perpendicular to the direction of the field, $f = 1/8$ at low values of $\varkappa a$ and $f \approx 1/4$ at high values of $\varkappa a$. For spherical particles, $f = 1/6$ at low values of $\varkappa a$ and $f = 1/4$ at high values of $\varkappa a$. Hence, the data of Fig. 7.21 are in complete conformity with Eq. (7.42), according to which the numerical coefficient is 1/4, regardless of the shape of particles, if the value of $\varkappa a$ is great, and with Eq. (7.47), according to which the numerical factor is 1/6 for spherical particles having a small value of $\varkappa a$.

Henry also analysed the dependence of the quantity f on the electric conductivity of the dispersed phase which completely changes the

distribution of the electric field near the particles. In Fig. 7.21, the dotted line denotes the values of the coefficient f as a function of $\varkappa a$ for spherical electroconductive particles. The distribution of the field does not affect the quantity f when the electric double layer is very thick ($\varkappa a \ll 1$) but, as the layer thickness diminishes, the coefficient decreases and approaches zero. However, the effect of electric

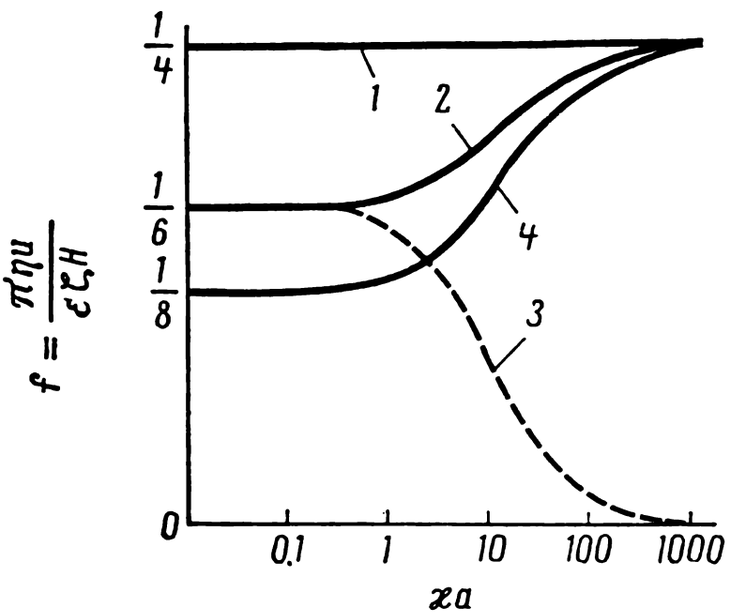

Fig. 7.21. Dependence of the quantity f on $\varkappa a$ for the particles:
1—cylindrical particle (its axis is parallel to the field) which does not conduct current; *2*—spherical particle which does not conduct current; *3*—spherical particle which conducts current; *4*—cylindrical particle (its axis is perpendicular to the field) which does not conduct current

conductivity of the colloidal metal particles can in practice be neglected in most cases because it is almost completely eliminated by surface polarization. In this case, the particle acts as if it were made of a non-conducting substance.

Therefore, in order to select a correct numerical coefficient in Henry's equation, it is necessary to know the dimensions of a particle, its shape (cylindrical, spherical), the thickness of the electric double layer, and whether the dispersed phase is a conductor or a dielectric. The dimensions and shape of a particle are determined experimentally by optical or other methods. Electric conductivity of the dispersed phase is usually known. The thickness of the electric double layer or, what is the same, the ionic atmosphere can be calculated by Eq. (7.5), according to the theory of strong electrolytes.

When the external electric field is applied, the moving charged particle is subjected not only to electrophoretic retardation, but also to *electric relaxation*. According to the electric theory of electrophoresis, the electric field of the double layer and the external electric field are assumed to be simply superimposed on one another. But, in fact, this is not so because the particle and the external part of the double layer move in opposite directions, and the initial symmetry

of the double layer relative to the particle is upset. Owing to electric conductivity and diffusion, the double layer tends to restore symmetry, but this takes time (relaxation time), and therefore the external part of the double layer remains behind the moving particle. As a result, an additional electric field originates which tends to move the particle in the opposite direction and thus affects the rate of electrophoresis.

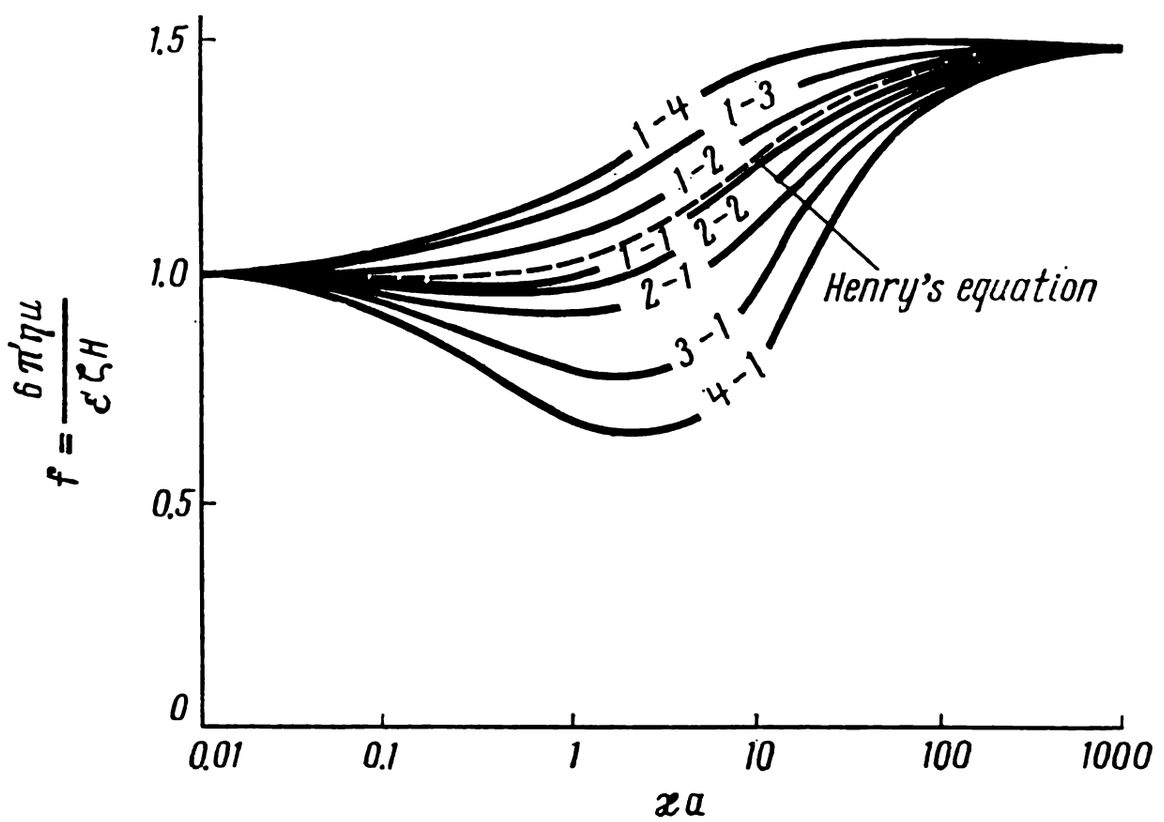

Fig. 7.22. Effect of relaxation and various types of electrolytes on the electrophoresis of colloidal particles having a negative ζ-potential equal to 50 mV
The type of electrolyte is denoted by figures on the curves: the first figure characterizes the valency of a cation, and the second, the valency of an anion

While not going into details concerning the effect of electric relaxation on the rate of electrophoresis, let us only note that, according to Oberbeek, the relaxation effect depends on the ζ-potential, the quantity $\varkappa a$ and the valency of electrolyte ions which are present in a system. Fig. 7.22 illustrates the effect of electric relaxation for spherical colloidal particles having a negative ζ-potential equal to 50 mV and various types of electrolytes. The values of $\varkappa a$ are plotted on the abscissa, and those of the quantity f', on the ordinate; in order to obtain correct results, the rate of electrophoretic transfer calculated by Hückel's equation (7.47) should be multiplied by f'. The dotted curve characterizes a change in the rate calculated by Henry's equation without taking account of relaxation.

Data in Fig. 7.22 show that the relaxation effect is inconsiderable at low and high values of $\varkappa a$. The curves are arranged differently, depending on the type of electrolytes. Electrophoresis of negatively

charged particles is retarded by symmetric electrolytes and electrolytes having polyvalent cations. Conversely, polyvalent anions accelerate the electrophoresis of negatively charged particles.

The correction for relaxation increases rapidly with the electrokinetic potential and ionic valency. But when the values of the electrokinetic potential are below 25 mV or when electrolytes having monovalent cations and anions are used, the relaxation effect is small and the correction for relaxation does not have to be introduced in Henry's equation because it is not higher than 3 per cent in this case.

The rate of electrophoresis can be affected, not only by electrophoretic retardation and electric relaxation, but also by the state of aggregation of the dispersed phase. For example, the rate of electrophoretic transfer of liquid particles when all other conditions of electrophoresis are the same is equal to the mobility of solid particles only when, as a result of adsorption of surfactants, the surface of a drop becomes stationary and this makes the liquid particle behave like a solid one. In general, liquid particles having sufficiently high conductivity travel faster than solid ones in electrophoresis because: (1) friction of the surface of a liquid particle is always less than that of a solid sphere of the same dimensions since liquid drops may become deformed when the medium moves; (2) the electric double layer at the liquid-liquid interface originates in both phases, and the part of it that is on the drop makes the liquid circulate within the drop, which affects the rate of electrophoresis.

A. Frumkin determined the electrophoretic mobility of a drop of mercury. He has shown that the drop is completely polarized and therefore its behaviour is similar to that of a non-conductor. However, polarization changes surface tension at the poles of the drop, causing mercury to move along its surface. If the drop is charged positively (this is the ordinary case), the charge at the surface of the drop near the pole facing the positive electrode diminishes and surface tension grows in this place; an opposite phenomenon is observed at the other pole of the drop. As a result of the difference in surface tensions, mercury moves within the drop; this is schematically illustrated in Fig. 7.23. The arrows within the drop show the motion of mercury, and those outside, the flow of the dispersion medium. The large arrow under the illustration denotes the direction in which the entire drop moves. The motion of mercury should accelerate the transfer of a particle to the negative electrode. Such circular movements may increase the rate of transfer of a drop by several orders in comparison with the ordinary rates of electrophoresis.

Now let us briefly consider the basic features of the principal electrophoretic methods because the technical details of experimental techniques are presented in the relevant practical-instruction manuals of colloid chemistry. Since electrophoresis is similar to electrolysis,

its rate can be often determined by the same methods as those used to estimate the mobility of ordinary ions; this can be done, for example, by determining the transport numbers, measuring the rate of movement of the interface, by using analytical methods, and employing the microscope or the ultramicroscope.

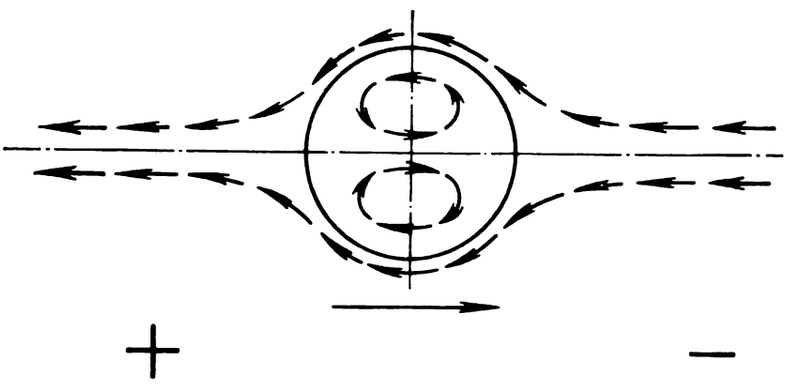

Fig. 7.23. Motion of liquid within a mercury drop in electrophoresis

The Hittorf method. This method is similar to the one used for determining the transport numbers of ions. An electric current is passed for a certain length of time through a colloidal solution put in a vessel, and then samples of the solution are taken from various places for determining analytically the amount of the dispersed phase that has moved to one of the electrodes. Apparently, this amount m is directly proportional to u, the rate of the electrophoretic transfer, c, the concentration of the dispersed phase, I, the intensity of current, and τ, the time during which current is being passed, and it is inversely proportional to γ, the electric conductivity of a liquid, i.e.,

$$m = ucI\tau/\gamma \tag{7.49}$$

The rate of electrophoresis can be determined by transforming this equation to

$$u = \gamma m/(cI\tau) \tag{7.50}$$

This method, when used for colloidal systems, is especially precise because of the large mass of the dispersed phase per unit charge. However, it is used rather rarely in practice. P. Tattje used Hittorf's method not only for determining the electrophoretic rate, but also for finding the mobility of counterions.

The moving boundary method. This method is used widely owing to its simplicity. It is based on the observation of the rate at which the boundary between the cloudy or coloured colloidal solution and the clear, colourless colloid-free dispersion medium (supernatant liquid) moves under the action of the electric field. To study the clear colourless sol, special techniques are used for making the boundary visible, such as illumination by ultraviolet light.

Many devices were proposed for determining the moving boundary. One such device, very simple in design, is Coehn's apparatus (Fig. 7.24). It is a wide glass U-tube, each limb of which has at the bottom a glass cock, the diameter of whose opening is equal to the inner diameter of the tube. The upper parts of both limbs are graduated, and the large division is equal to one centimetre. Platinum electrodes are put into both limbs. The colloidal solution is introduced into the device through a funnel which is connected to the lower part of the U-tube by a narrow glass tubing with a cock.

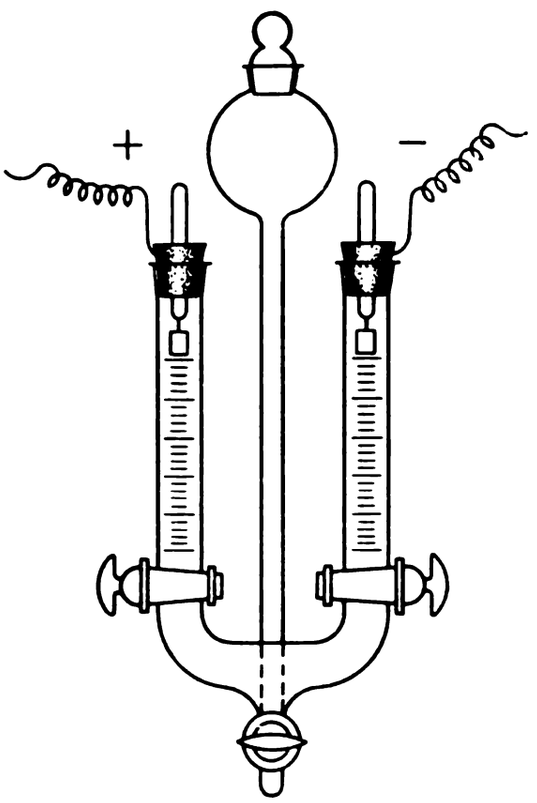

Fig. 7.24. Scheme of Coehn's electrophoresis apparatus

The apparatus is assembled for operation in the following way. The test colloidal solution is poured through a funnel into the lower part of the U-tube when the cocks are open in such a quantity that its level is higher than the cocks. Then, the cocks on both limbs of the U-tube, and the cock on the tubing connecting the apparatus with the funnel are closed. The liquid in both limbs above the cocks is removed with a pipette (or by tilting the apparatus). Definite quantities of the pure dispersion medium are introduced into both limbs with a pipette so that its levels have the same height and are 3-4 cm higher than the graduation. Then, an electrode inserted through a rubber plug is put into each limb, and cocks are carefully opened in both limbs. Now, the apparatus is ready for operation.

The determination consists in the measurement of the time (with a stopwatch) taken by the interface between the colloidal system and the dispersion medium to move by a height of one centimetre in one of the limbs after a direct current of definite intensity is switched on. Several such determinations are performed without switching off the current, and their arithmetic mean value is taken for calculating the electrophoretic rate. Simultaneously, the voltage on the electrodes is recorded by means of a voltmeter which is also connected to the electric circuit. At the end of the experiment, the distance between both electrodes within the tube is also measured so that the potential gradient of the external field can be calculated.

In more advanced apparatus, the limbs are graduated both above and below the cocks. This makes it possible to work with colloidal

systems which are less dense than the colloid-free dispersion medium, for example, with emulsions in which the density of the dispersed phase (usually hydrocarbon) is smaller than that of the dispersion medium (water). In this case, the colloid-free dispersion medium is located at the bottom, and the colloidal solution, on the top.

Non-polarizing electrodes are used to prevent electrode polarization. To stop electrolysis products from getting into a system, electrodes are usually put into wide vessels, that are connected with the limbs of the apparatus by glass tubings filled with agar gel which contains potassium chloride, as is done in electrochemistry in measuring pH.

For greater precision, the movement of the interface between the colloidal solution and the auxiliary liquid is observed with a short-focus optical tube fixed to a cathetometer.

In selecting the dispersion medium, its composition and properties should be taken into account. Unlike the colloidal solution, it must be clear or colourless; it must not affect the ζ-potential of colloidal particles which pass over into it from a sol; it must have electric conductivity which is equal to, or somewhat greater than, that of the colloidal system. If these requirements are met, a sharp boundary is formed between the sol and the auxiliary liquid, and corrections do not have to be made for their different electric conductivity when the external potential gradient is being calculated.

A sol ultrafiltrate or the dispersion medium obtained by coagulating the colloidal system by freezing is often used as a superhatant liquid. However, if concentrated colloidal solutions with a small content of electrolytes are being investigated, the superhatant liquid thus prepared has different electric conductivity in comparison with the sol. In this case, when the electrophoretic rate is calculated, it is necessary to make a correction for the distribution of intensity in the electric field, and this is sometimes difficult to do.

The Tiselius method. This method is, in principle, the same as the moving boundary method, but it has many specific features. Measurements are made by this method in a device which is an improved version of Coehn's apparatus. To create a sharp boundary between the colloidal solution and the superhatant liquid in Tiselius apparatus, not the cocks, but the shift of ground-in parts of the U-tube along each other, are used. Fig. 7.25 shows a section of the main part of the apparatus which corresponds to the U-tube of Coehn's apparatus. The lower part of the tube must already be filled with the test sol when the upper part is filled with the colloid-free solution. The cross-section of the U-tube is not round, but rectangular, and this makes it easier to observe the boundary movement. Moreover, under such conditions, the liquid acquires more rapidly the temperature of the water thermostat which is a part of the apparatus. Determinations

are as a rule performed at +4 °C which corresponds to maximum water density. Under these conditions, liquid density changes very little

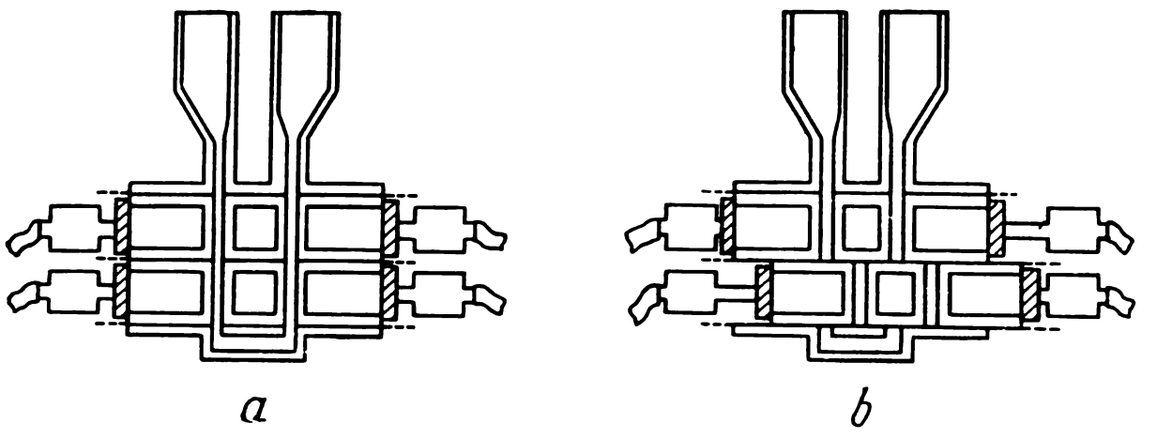

Fig. 7.25. U-tube of Tiselius apparatus (side view):
a—working position; *b*—filling position for the upper part

at small temperature fluctuations, and therefore convection currents are not formed and the interface is diffused inconsiderably. The working electrodes are placed in the wide electrode vessels so that elec-

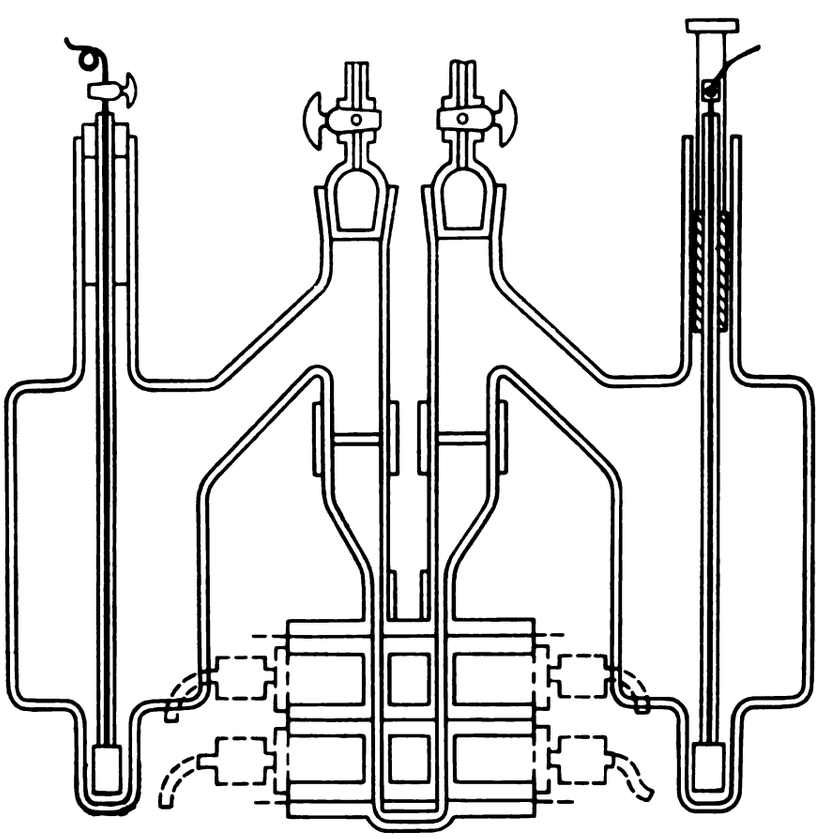

Fig. 7.26. Complete Tiselius apparatus

trolysis products do not contaminate the sol. Fig. 7.26 shows Tiselius apparatus when it is assembled. The boundary movement is determined by the difference in refractive index of the test solution and of its ultrafiltrate which is used as a superhatant liquid.

The ingenious optical system of Philpot and Svensson makes it possible to study the distribution of the gradient of refractive index in the moving boundary region by a graphic method. In this method, the flat light beam passing through the U-tube is photographed or observed, so that all the irregularities of distribution of a colloidal substance in a liquid column are registered. If there is no gradient of refractive index, the light beam produces a single continuous vertical line on a photographic plate owing to a special arrangement of lenses. If such a gradient exists, there will be a peak for it on the photographic plate. The nature of this peak shows the position of the interface in the liquid column, its sharpness, and the difference in concentrations on both sides of the interface.

Tiselius' method is widely used in studying proteins and other high molecular weight electrolytes because it can help not only to determine the electrophoretic rate, but also to separate a mixture of high molecular weight substances into individual components. Indeed, if the test solution has several components with different electrophoretic mobilities, the front of movement of the more mobile components will overtake that of the less mobile ones, and there will be the same number of boundaries as there are components in a mixture.

Paper electrophoresis. The Tiselius apparatus is very intricate. A simpler method, also proposed by Tiselius, is used now to study proteins. It is called paper electrophoresis, and is effected in the following way. A drop of the test colloidal solution is put in the centre of a strip of thick, homogeneous filter (chromatographic) paper which is impregnated with a buffer solution of a definite pH value. The potential gradient is then applied to the strip of paper. Under the action of the electric field being formed, components which are contained in the drop and have different electrophoretic mobilities move along the strip at different rates. After a certain lapse of time, the components are distributed on paper as zones which are at different distances from the starting point and are equal in number to the components contained in the drop. The strip is dried and heated to denature and fix the proteins on it. Then it is stained with suitable reagents to develop components distributed along the strip. In this method, paper serves the purpose of eliminating the diffusive and convective mixing of proteins in electrophoresis.

The method of paper electrophoresis can be used not only to study the composition of mixtures of high molecular weight substances, but also to isolate individual components. Accordingly, the strip of paper is cut into pieces without heating it, and individual, already separated components are extracted from them. The theory of this method in which surface and adsorption phenomena play a considerable role is not yet sufficiently elaborated.

The microscopic and ultramicroscopic methods. These methods of determining electrophoretic mobility consist in the estimation of the rate of movement of individual colloidal particles in the electric field by means of a microscope or an ultramicroscope. This method has several advantages over the moving boundary method. First, when an investigation is being made with a microscope, particles are in the same medium, and there is no interface between the colloidal system and colloid-free liquid. Second, very small quantities of a solution are necessary for a determination. The shortcoming of the method is that it cannot be employed in the case of particles in solutions having a considerable concentration of the dispersed phase because the movement of a particle cannot be observed in such solutions. The dilution of such a system with a foreign liquid always affects the ζ-potential.

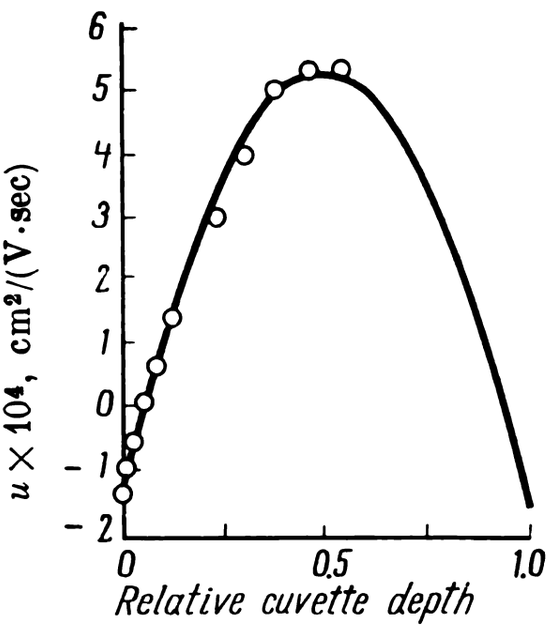

Fig. 7.27. Observed (circles) and theoretical (curve) rates of the electrophoretic transfer of oil droplets at different depths of the cuvette

When the microscopic or the ultramicroscopic method is used, the test colloidal solution is poured into a closed, rectangular or cylindrical, cuvette with electrodes, and the time taken by a particle to move a certain distance is measured. Since particles are in Brownian motion, the arithmetic mean value of several determinations is taken. Moreover, the liquid in the cuvette is in electroosmotic motion along the cuvette walls. But since the cuvette is closed, a return current of the liquid is established in the centre of the cuvette, and the transfer of the liquid in the cuvette is thus on the whole equal to zero. The rate of motion of the liquid in the cuvette is superimposed on the electrophoretic rate of motion of particles, and the value found is the algebraic sum of these rates. Of course, the value of this sum depends on the location of a particle in the cuvette. An example of this are the results of the work of Ellis who determined the relationship between the rate of motion of oil droplets in a rectangular cuvette and the height at which the droplets were located relative to the cuvette bottom. These data are represented as circles in Fig. 7.27 (the parabola corresponds to the theoretical rate of electrophoresis).

To calculate the true electrophoretic rate, we may take the mean value of the rates observed along the plane of the cross-section of a cuvette. But this is difficult, and it is more practical to measure the

electrophoretic rate in the place of the cross-section of the cuvette where the rates of electroosmosis and return flows are equal to each other and where, as a result, the liquid is at rest. The theory by means of which such places are found in a cuvette was proposed by Smoluchowski, and it is presented in courses in practical colloid chemistry. In a cylindrical cuvette, the layer where the rate of motion of a liquid is zero lies at a distance of 0.148 of its diameter away from

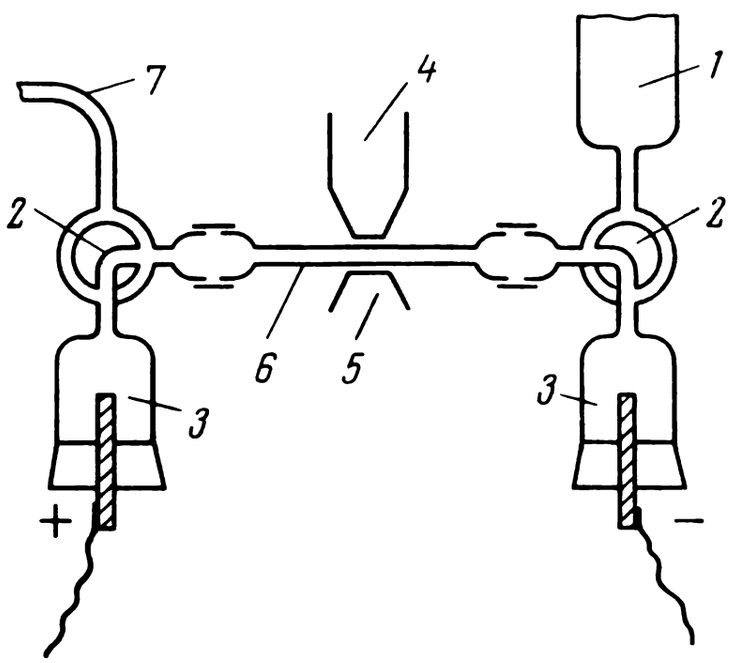

Fig. 7.28. Scheme of the microelectrophoresis apparatus proposed by Abramson: *1*—funnel for the test solution; *2*—three-way cocks; *3*—non-polarizing electrodes; *4*—objective of the microscope; *5*—condenser; *6*—cuvette; *7*—outlet

the wall. There are two such layers in a rectangular wide cuvette, and each of them is at a distance of 0.212 of its height. In other words, these layers correspond to about 1/5 and 4/5 of the height of the cuvette.

Several devices and apparatus have been proposed for the microscopic and ultramicroscopic determinations of the electrophoretic rate. The simplest of them are cuvettes consisting of a glass slide and a cover glass between which are two thin platinum plates pasted to both glasses and serving as electrodes. After putting a sol into this cuvette, its side slits are plastered up with vaseline. Of course, there is the possibility that electrodes may be polarized and the products of electrolysis may get into a sol in such cuvettes.

Fig. 7.28 shows a scheme of the microelectrophoresis apparatus proposed by Abramson. The apparatus consists of rectangular flat glass cuvette *6* connected with glass tubes that have three-way cocks *2*. One of these cocks links the cuvette with funnel *1*. Using the funnel and cocks, the cuvette is first washed and then filled with the test colloidal solution. Immediately before making a measurement, the cuvette is disconnected from the funnel and outlet *7* by turning

the cocks, and is connected to non-polarizing electrodes 3 by zinc rods in a saturated solution of zinc sulphate.

Electrophoresis is as a rule effected by direct current, and a switch is inserted into the circuit of the apparatus for changing the direction of the current. As early as 1919 Svedberg used alternating current to determine the electrophoretic rate; when this current is used, particles oscillate and are seen in the dark-field ultramicroscope as bright lines of definite length. The electrophoretic rate can be calculated when current frequency is known and the length of the bright line is measured.

The given method of determining electrophoretic rate can be applied also to solutions of high molecular weight compounds whose molecules are not visible under the ultramicroscope. For this purpose, small particles of quartz or coal which adsorb on themselves a high molecular weight substance are introduced into a solution. The electrophoretic mobility of such particles has been found to be the same as that of free macromolecules because, according to the Helmholtz-Smoluchowski equation, the electrophoretic rate does not depend on the particle dimensions. However, the value of the ζ-potential calculated by such measurements is not accurate because a double layer which has a constant potential hardly exists here.

Electroosmotic methods. The ζ-potential can be calculated not only by the electrophoretic rate, but also by the electroosmotic rate of movement. Although the electroosmotic rate can be determined directly, in order to calculate the ζ-potential, it is far more convenient to measure the volume of liquid which passes through a capillary or a porous membrane in electroosmosis, or to estimate pressure which develops as a result of the electroosmotic motion of liquid.

Volume of the liquid transported by electroosmosis. Apparently, the following expression is valid for the volume V of a liquid which passes through a capillary having radius r per unit time:

$$V = \pi r^2 u = \frac{\pi r^2 \varepsilon \zeta H}{4\pi\eta} = \frac{r^2 \varepsilon \zeta H}{4\eta} \qquad (7.51)$$

In the case of the electroosmotic flow of a liquid through a capillary, the motive force has an electric nature and acts on the peripheral parts of the cylinder of the liquid which fills the capillary where free counterions are concentrated. As a result, when the electric field is applied, the rate of motion of a liquid in a capillary will first be maximum at the wall of the capillary and minimum at its axis. The rates then become equal owing to friction between liquid layers; at a steady state of flow, the liquid moves at the same rate throughout the capillary. The establishment of a steady flow in electroosmosis is schematically illustrated in Fig. 7.29*a*.

In electroosmosis, the nature of liquid motion is directly opposite to what is observed when liquid moves under the action of hydrostatic pressure when the rates of liquid motion are equal everywhere at the beginning of flow. In the latter case, friction at the wall gradually makes the flow rate of peripheral layers to become smaller than that of the central ones, and the rate curve in the case of a steady state of flow assumes the shape of a parabola (Fig. 7.29*b*).

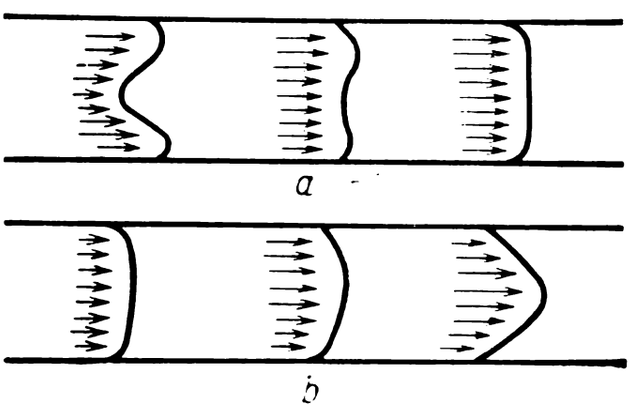

Fig. 7.29. Diagram explaining the establishment of a steady state of liquid flow in a capillary:
a—in electroosmosis; *b*—under the action of hydrostatic pressure

According to Smoluchowski, the porous membrane can be regarded as the sum of capillaries with a total sectional area of s. The volume of a liquid which electroosmotically flows through the membrane per unit time is then expressed by the equation

$$V = su = \frac{s\varepsilon\zeta H}{4\pi\eta} \tag{7.52}$$

i.e., is directly proportional to the cross-section of capillaries, the dielectric constant, the ζ-potential and the electromotive force, and inversely proportional to the viscosity of the liquid.

According to Ohm's law:

$$E = IR \tag{7.53}$$

where E = potential gradient;
I = current intensity;
R = electric resistance of a system.

The electric resistance of an electrolytic solution is equal to

$$R = \frac{L}{\gamma s} \tag{7.54}$$

where L = thickness of the solution layer;
s = cross-sectional area;
γ = specific electric conductivity of the solution.

Substituting the given expression for R in Eq. (7.53), we obtain

$$E = IR = \frac{IL}{\gamma s} \tag{7.55}$$

Using this expression for E, the gradient of the external potential can be expressed as

$$H = \frac{E}{L} = \frac{IL}{s\gamma L} = \frac{I}{\gamma s} \tag{7.56}$$

Substituting the value of the gradient in Eq. (7.52), we have

$$V = \frac{s\varepsilon\zeta H}{4\pi\eta} = \frac{s\varepsilon\zeta I}{4\pi\eta\gamma s} = \frac{\varepsilon\zeta I}{4\pi\eta\gamma} \tag{7.57}$$

Since Eq. (7.57) includes neither L nor s, it is evident that when current intensity is constant, the volume of a liquid which has passed through the membrane does not depend on the cross-sectional area and on the capillary length. The correctness of this equation was confirmed by Wiedemann's experiments.

It is easy to find the value of the ζ-potential using Eq. (7.57):

$$\zeta = \frac{4\pi\eta\gamma V}{\varepsilon I} \tag{7.58}$$

By analogy with Eq. (7.46), the right-hand member of this equation must be multiplied by 300^2 in order to express the ζ-potential in volts. Eq. (7.58) then becomes

$$\zeta = \frac{4\pi\eta\gamma V 300^2}{\varepsilon I} \tag{7.59}$$

Thus, in order to determine the value of the ζ-potential by electroosmosis, it is necessary to find the volume of a liquid transferred through a capillary or a porous membrane, and also the electric conductivity of a solution and the intensity of the current by which electroosmosis is effected. The other quantities are usually taken from handbooks.

In using Eq. (7.58), *surface conductivity* must be taken into account. This phenomenon is caused by the ions near the interface which change the composition of the medium and, consequently, the specific electric conductivity of a solution at the interface. If the capillary radius is large enough in comparison with the thickness of the layer near the wall where surface conductivity is exhibited, the average electric conductivity of a solution remains almost the same as that in its volume, and the quantity γ in Eq. (7.58) is the specific electric conductivity of the solution. If the capillaries are thin, this condition is not met and γ becomes a function of the capillary radius. In this case, instead of Eq. (7.58), it is necessary to use the

equation

$$\zeta = \frac{4\pi\eta\,(\gamma + O\gamma_s/s)\,V}{\varepsilon I} \tag{7.60}$$

where O = length of the circumference of a capillary;
s = its section;
γ_s = surface conductivity.

The factor $(\gamma + O\gamma_s/s)$ in the numerator of Eq. (7.60) is inserted instead of the quantity γ because $\bar{\gamma}$, the electric conductivity of a liquid which fills a capillary, is equal to the sum of the electric conductivities (reciprocals of resistances) of the volume of the liquid and of the layer near the surface:

$$1/\bar{R} = 1/R + 1/R_s \tag{7.61}$$

where $1/\bar{R} = \bar{\gamma}s/L$, $1/R = \gamma s/L$, and $1/R_s = \gamma_s O/L$; it is taken that the thickness of the layer having surface conductivity is small in comparison with the capillary radius. Hence, total electric conductivity $\bar{\gamma}$ is

$$\bar{\gamma} = \gamma + \frac{O\gamma_s}{s} \tag{7.62}$$

The quantity $O\gamma_s/s$ apparently represents an increase in the electric conductivity of a liquid in a capillary as a result of surface conductivity. Since $O/s \sim 1/r$, the correction for surface conductivity is not needed when capillaries have a sufficiently large radius.

Comparing Eqs. (7.58) and (7.60) and taking into account that the quantity $O\gamma_s/s$ is always positive, we can see that, owing to surface conductivity, the true values of the ζ-potential in the case of sufficiently thin capillaries are always higher than the ones calculated without a correction for surface conductivity. This was confirmed by experiments. Fig. 7.30 gives the results of the experiments carried out by I. Zhukov. He determined the ζ-potential by measuring streaming potential with and without regard to surface conductivity. Diaphragms of quartz and corundum were used as porous membranes, and a weak solution of potassium chloride was used as a liquid. We can see from the nature of the curves that the values of the ζ-potential determined without regard to surface conductivity diminish when diaphragms having pores of a small section are used; when a correction is made for surface conductivity, almost the same values of the electrokinetic potential are obtained in the whole range of tested capillary radii. Consequently, the radius of capillary pores must always be taken into account when the ζ-potential is being determined electroosmotically or by the flow method.

The foregoing correction characterizes the surface conductivity of an individual capillary whereas in practice real objects are porous

bodies in most cases. To determine the correction for the surface conductivity of porous bodies, the electric resistance of the membrane in the test and standard solutions is measured and the quantity γ_s is calculated by the data obtained.

A phenomenon connected with surface conductivity is *capillary superconductivity* discovered by D. Fridrikhsberg. If a tube containing a solution which conducts current is partitioned with a porous diaphragm made of a non-conducting material, the electric resistance

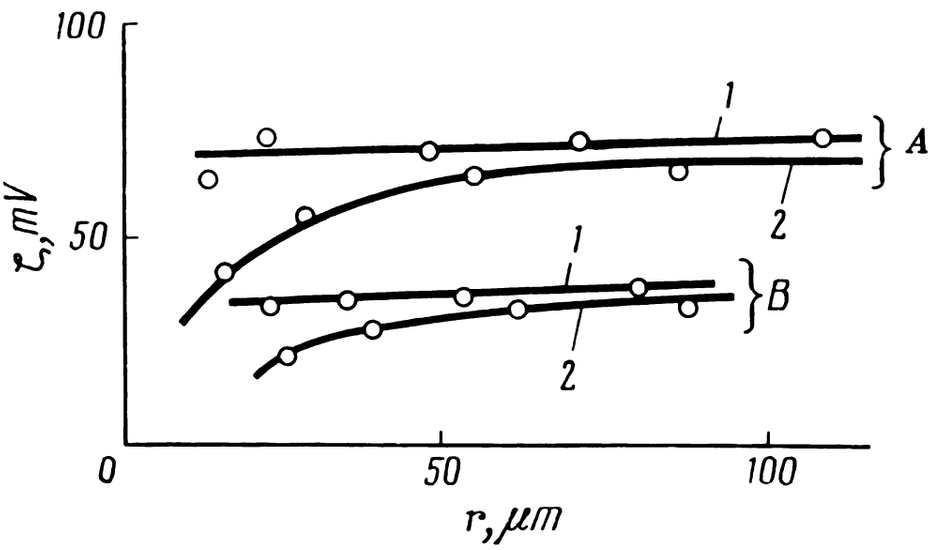

Fig. 7.30. Dependence of the ζ-potential on the capillary radius r with regard (*1*) and without regard (*2*) to surface conductivity:
A—quartz membrane; *B*—corundum membrane

of a system increases because a part of the tube section is occupied with a dielectric. However, if a layer possessing surface conductivity is formed at the surface of the diaphragm capillaries, the total conductivity of fine-capillary porous bodies in dilute electrolytic solutions increases owing to this conductivity. At first glance, there will be the paradoxical effect of a decrease in electric resistance when a diaphragm made of a dielectric is put into the tube.

Let us now deal briefly with apparatus used for determining the ζ-potential by the volume of the liquid transported by electroosmosis. In all such apparatus, electroosmosis is effected not with a single capillary but with a porous solid diaphragm.

Fig. 7.31 illustrates an electroosmosis apparatus proposed by J. Perrin. Porous plug *1* of the test substance is put in the central part of the glass U-tube which is connected to the side limbs by means of ground-glass joints. Both side limbs have platinum electrodes *2* to which direct current whose voltage is at least 40-50 V is applied. The right-hand side limb has funnel *3* with a cock for filling the apparatus with a dispersion medium, and the left-hand limb has cock *4* for discharging the liquid from the apparatus. A horizontal graduated capillary tube *5* is connected to the right-hand limb to observe the movement of a liquid in it.

Before a determination, the apparatus is filled with a liquid so that the pores of plug *1* no longer contain air and the meniscus of the liquid in the left-hand part of the capillary tube *5* is in a permanent position. Then, current is switched on in such a direction that the meniscus in capillary *5* moves from left to right, and its

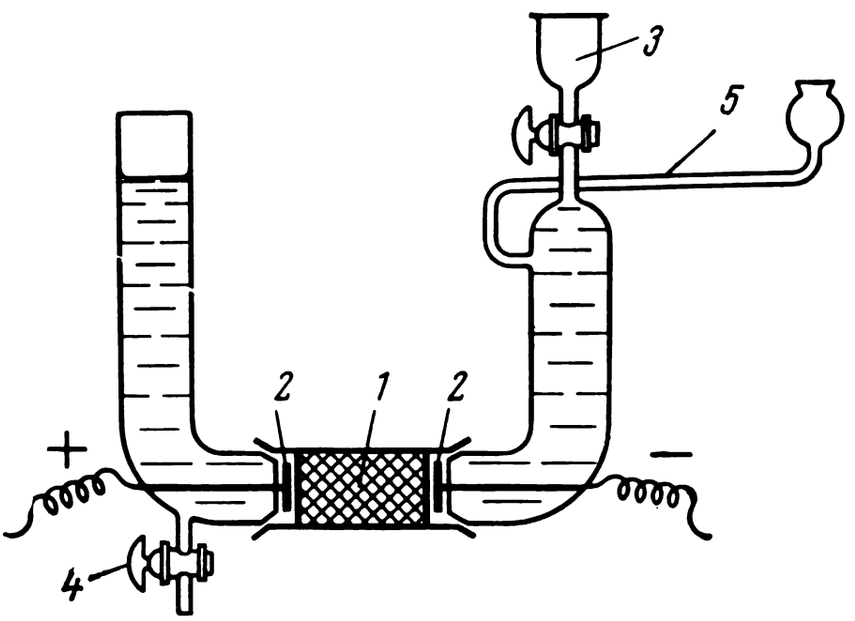

Fig. 7.31. Scheme of Perrin's electroosmosis apparatus:
1—plug of the test substance; *2*—electrodes; *3*—funnel; *4*—cock; *5*—graduated tube

rate of motion is read with a stopwatch. Current intensity is simultaneously measured with a milliammeter which is connected to the electric circuit of the apparatus. A shortcoming of the apparatus is the polarization of electrodes and the formation of electrolysis products which may penetrate into the plug capillaries and thus cause an error in the results.

In more advanced apparatus, non-polarizing electrodes are used, which are sufficiently far away from the plug or are connected to it with agar bridges. In the electroosmosis apparatus proposed by Umetsu, the porous plug is placed in the vertical glass tube having a glass network in its lower part.

A plug of the necessary height is obtained by filling the tube with a powder suspension and then sucking off the liquid with a water-jet pump. Afterwards, the apparatus is filled with a solution, agar bridges are inserted in order to connect the plug with non-polarizing electrodes, and direct current is switched on. The rate of electroosmosis is determined by a graduated glass capillary, and the initial position of the meniscus is established by slightly opening a special side cock.

Determination by electroosmotic counter pressure. In this method, not the volume of a liquid which in electroosmosis passes through a capillary or a porous membrane per unit time is measured, but

the counter pressure generated by the electroosmotic displacement of a liquid. Accordingly, the limb of the electroosmotic apparatus into which a liquid enters should terminate in a vertical or oblique tube; the tube serves to establish the height of the liquid column that counterbalances the electroosmotic force. The pressure of this column forces the liquid to flow through the capillary or the porous plug in the opposite direction until gravity and osmotic pressure are in equilibrium.

The equation for calculating the ζ-potential is derived on the basis of the fact that, in an equilibrium state, the volume V_1 of a liquid which enters a capillary per unit time under the action of the electroosmotic force is equal to the volume V_2 of a liquid which flows out of the capillary during the same length of time under the action of hydrostatic pressure-head P. Volume V_1 is expressed by Eq. (7.51)

$$V_1 = \frac{r^2 \varepsilon \zeta H}{4\eta}$$

For V_2, according to Poiseuille's law, we may write

$$V_2 = \frac{\pi P r^4}{8\eta l}$$

where l is the capillary length.

In the equilibrium state $V_1 = V_2$ and, consequently,

$$\frac{r^2 \varepsilon \zeta H}{4\eta} = \frac{\pi P r^4}{8\eta l} \tag{7.63}$$

whence

$$P = \frac{2\varepsilon \zeta H l}{\pi r^2} \tag{7.64}$$

Quincke and Wiedemann discovered that electroosmotic pressure P is proportional to the gradient of the outer potential H and inversely proportional to r^2; this completely conforms to Eq. (7.64).

From Eq. (7.64) it is easy to find the value of the ζ-potential by pressure P or by the height to which a liquid rises in the tube.

Such a method may be used (when surface conductivity is absent) also in the case of electroosmosis through a porous plug. However, it is not widely used in practice.

Comparison of the ζ-potential values found by different methods. The determination of the electrokinetic potential is complicated during both the organization of an experiment and the calculation of the ζ-potential from experimental data. Even recently, scientists did not take account of the effect of surface conductivity, electrophoretic retardation and electric relaxation; therefore, only a few

of the many investigations of electrokinetic phenomena gave reliable values of the ζ-potential.

The best proof of the accuracy of the values of the ζ-potential which are determined with regard to the required corrections is the identity of these values found in the case of various electrokinetic phenomena.

A. Rutgers and P. Wijga determined the values of the ζ-potential by the streaming potential and by electroosmosis and obtained the

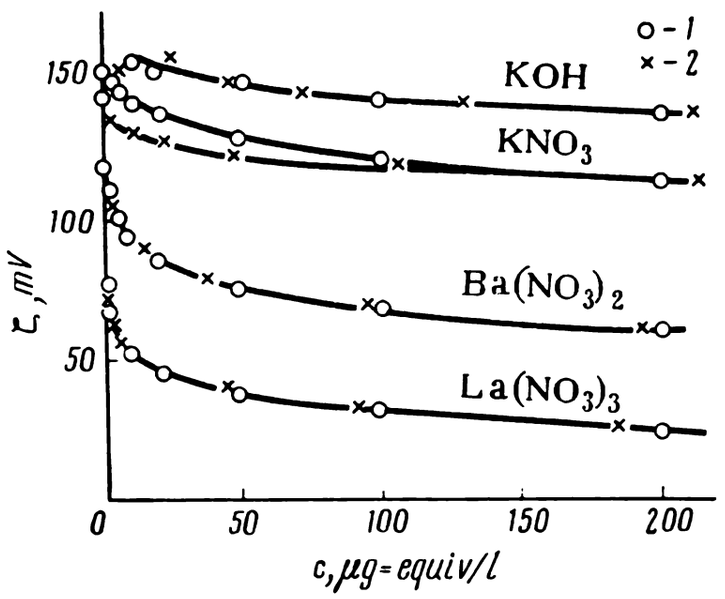

Fig. 7.32. Dependence of the ζ-potential of the Pyrex capillary wall on the concentration of an electrolyte:

1—data calculated according to the results of elecroosmotic determinations; *2*—data obtained when the streaming potentials were being determined

same values. Fig. 7.32 represents the relationship between the ζ-potential of the wall of a glass capillary and the concentration of an electrolytic solution filling the capillary. As we may see, the values of the ζ-potential which are calculated from electroosmotic data and from data obtained when the streaming potential was being determined are on the same curve. The discrepancies in the data for KNO_3 are due to the different treatment of the capillary used in this experiment.

The equivalence of the values of the ζ-potential found by electrophoresis and electroosmosis has also been confirmed many times. For instance, in his scrupulous experiments in the electroosmosis and microelectrophoresis of protein-covered particles, Abramson took account of all the necessary corrections and established the equality of the values of the ζ-potential found by both techniques. The ζ-potential which was found by determining streaming potentials turned out to be equal to the ζ-potential calculated from electrophoretic data.

Thus, although the small amount of experimental material is not always absolutely convincing, it may be asserted that all the

three electrokinetic phenomena are equivalent, and that the values of the ζ-potential which were determined by these three methods are the same.

6. PRACTICAL IMPORTANCE OF ELECTROKINETIC PHENOMENA

Electrokinetic phenomena are of great practical significance. They may be used to determine a very important characteristic of disperse systems, i.e., the ζ-potential; complex mixtures of natural proteins and other macromolecular electrolytes can be fractionated and characterized by means of electrophoresis.

Electrokinetic phenomena are widely used not only in research, but also in industry. In particular, electrophoresis is used for depositing a thin layer of colloidal particles on the surface of a conducting material to obtain uniform coverings whose thickness is easy to control in alcohol, acetone, and other media; this precludes the evolution of gases on electrodes even when current intensity is high and electric conductivity of a liquid is low. Electrophoresis is used to deposit current-conducting coverings in the production of isolated heating spirals and activated cathodes for radio tubes which consist of a metal wire covered with a thin layer of oxide of an alkaline-earth metal.

Electrophoresis is also used for covering metal parts with raw rubber by depositing its particles contained in latices (aqueous dispersions of raw rubber) on the surface of metal parts. In this process, negatively charged particles of latex move to the anode (an object that must be coated) and settle on it, forming a thick film. Fillers which strengthen raw rubber and vulcanizing agents can be preliminarily introduced into latex. Rubber coverings of high quality are thus obtained on the metal parts.

B. Deryagin, S. Dukhin and A. Korotkova revealed the mechanism of the formation of latex films by means of "ion deposition" which is used in the technological processes of latex treatment. This technique is effected by depositing a layer of a fixing agent which contains a salt having a polyvalent cation that is capable of astabilizing negatively charged particles of latex on a mould that is made of glass, porcelain, or metal; the mould is immersed in the latex, and a latex film of the required shape is formed on it.

The deposition of latex films on a mould is caused by the gelation of latex by ions which diffuse from the layer of a fixing agent into the depth of the latex. However, it is still not clear why the latex concentration at the surface of the mould considerably increases in the course of the process. According to these authors, the source of the forces which are capable of displacing latex particles towards

the mould are gradients of the electric and chemical potentials accompanying the diffusion of ions of an electrolyte contained in a fixing agent into the depth of a solution. In other words, the motion of suspended particles is caused by the electric field formed in electrolytic diffusion.

Since the ζ-potential of latex globules is usually negative, latex particles always move towards the mould when calcium chloride is used in ion deposition for which the coefficient of diffusion of a positive ion is less than that of a negative one. The transfer of charged particles under the action of the electric field formed in electrolytic diffusion was termed diffusio-phoresis by the authors.

The importance of electrophoresis in destruction of aerosols is treated in Chap. 11.

Electroosmosis is used in the dehydration of porous materials. For this purpose, a moist mass is placed between electrodes; water in the electric field formed moves to one of them, usually to the cathode where it runs off. Electroosmosis can be also used for dehydration (in combination with pressure) when filtration is being effected. The filter presses used for such dehydration are known in industry as electroosmotic filter presses. Many attempts have been made to use electroosmosis for dehydrating peat, but this problem is still unsolved because of the great expenditure of energy.

Quincke's proposal to use the streaming potential for obtaining electric energy has not still been realized in practice.

7. OTHER ELECTRICAL PROPERTIES OF COLLOIDAL SYSTEMS

Let us briefly consider now the electric conductivity and dielectric constant of lyosols because these properties are closely connected with electrokinetic phenomena and with the stability and coagulation of colloidal systems.

Electric conductivity of lyosols. Electric conductivity of a lyosol is a sum of electric conductivity of colloidal particles and electric conductivity of ions present in a system. Therefore, electric conductivity of a colloidal solution depends on the charge, number, and mobility of colloidal particles and ions which are in a sol.

Let us see a relationship which exists between electric conductivity of colloidal particles and that of ions present in a sol. Suppose that a sol contains 1 per cent by volume of the dispersed phase, and that the particle radius r is 50 Å and the ζ-potential is 100 mV in the dispersion medium for which $\varkappa$ is 10^5. By analogy with Eq. (7.31), we may write for the particle charge

$$Q = r\varepsilon\zeta\,(1 + \varkappa r) \tag{7.65}$$

If account is not taken of electric relaxation, the electrophoretic mobility of particles can be expressed by the relation

$$u_0 = \frac{\varepsilon\zeta}{6\pi\eta}$$

The number of particles ν contained per unit volume of a colloidal solution is

$$\nu = \frac{0.01}{{}^4/_3\pi r^3}$$

Electric conductivity γ_{coll} caused by colloidal particles will then be

$$\gamma_{coll} = Q\nu u_0 = r\varepsilon\zeta\,(1+\varkappa r)\,\frac{0.01}{{}^4/_3\pi r^3}\,\frac{\varepsilon\zeta}{6\pi\eta} = \frac{0.01\varepsilon^2\zeta^2\,(1+\varkappa r)}{8\pi^2 r^2\eta} \qquad (7.66)$$

If we substitute the values of $\varkappa$ and r, and the values of ε and η for water in the last equation and express electric conductivity in practical units, we obtain

$$\gamma_{coll} \approx 4\cdot 10^{-5}\ \text{ohm}^{-1}\cdot\text{cm}^{-1}$$

The electric conductivity of the dispersion medium, for which $\varkappa = 10^5$ is about 10^{-6} $\text{ohm}^{-1}\cdot\text{cm}^{-1}$. Thus, electric conductivity caused by the presence of colloidal particles in a sol can be measured if only the particles are not too large and the concentration of a sol is not too small.

W. Pauli and other scientists measured the electric conductivity of hydrosols by conductometric titration in order to determine the ion components of a system. As A. Rabinovich has shown, conductometric titration can be used not only to determine the number of counterions and, consequently, the charge of colloidal particles, but also to establish the localization and fixation of counterions in the double layer. Let us explain this by taking the following example.

Fig. 7.33 presents, in the form of schematic curves, the results of the conductometric titration of a hydrosol of arsenic sulphide (the potential-determining ion is HS^-, and the counterion is H^+) with the solutions of potassium hydroxide and barium chloride. As we may see, curve *1* for titration with a solution of KOH has a minimum because the counterion H^+ in the adsorption layer of the micelle is substituted by K^+ when the initial portions of the alkali are added; this causes the formation of the almost non-ionized molecule H_2O from the ions H^+ and OH^-. The electric conductivity of a system drops as a result of a decrease in the content of hydrogen ions which are very mobile. Later, the electric conductivity of a sol increases when more alkali is added after all the hydrogen ions are substituted. The number of bound hydrogen ions in a sol can be evaluated by the amount of alkali that corresponds to the minimum on the curve.

Curve *2* for titration with a solution of $BaCl_2$ does not have a maximum, and it consists of curvilinear and rectilinear segments. Since water is not formed in titration with $BaCl_2$, the curve cannot have a minimum, and electric conductivity gradually increases in the course of titration. Owing to the greater mobility of H^+ ions in comparison with Ba^{2+} ions, the electric conductivity of a sol at the beginning of titration grows more than it should as regards the amount of the electrolyte added, and that is why this segment is

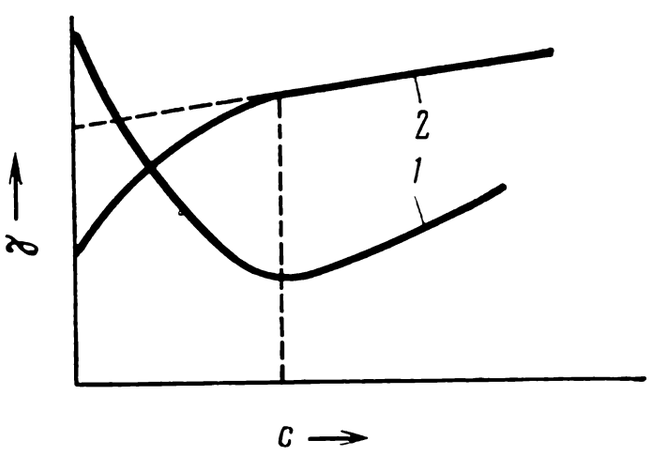

Fig. 7.33. Results of the conductometric titration of an arsenic sulphide sol: *1*—curve for titration with KOH; *2*—curve for titration with $BaCl_2$

curvilinear. The point of transition of the curvilinear segment to a rectilinear one that corresponds to the minimum on curve *1* for titration with KOH apparently conforms to the complete substitution of hydrogen ions by barium ions. A further addition of the barium chloride solution causes only a linear increase in electric conductivity.

In general, the same results are obtained in titration with both KOH and $BaCl_2$. All the H^+ ions in the adsorption layer are forced out of the micelle because of the high adsorption potential of barium ions.

Different results may be obtained when working with other hydrosols and electrolytes. For example, from the very beginning of titration of a mastic sol, electric conductivity is directly proportional to the amount of the electrolyte added. The rectilinear shape of the graph for conductometric titration indicates that the hydrogen ion is not displaced from the adsorption layer in this case.

Hence, conductometric titration can be used to find the nature of forces by means of which counterions are held in the adsorption layer. If the results of titration indicate that all the counterions of a micelle can undergo exchange, i.e., can be forced out of both the diffuse and the adsorption layers, then these ions are held in a micelle only by physical forces (electric and adsorption forces). Conversely, if a part of the counterions either is not forced out of the double layer

or is forced out with great difficulty, they are held in the micelle by forces which are similar in nature to chemical ones.

The high frequency and high voltage of a current affect the electric conductivity of hydrosols in a similar way as they affect the electric conductivity of normal electrolytes. But this effect is stronger for colloidal systems because it is connected with electrophoretic retardation and electric relaxation whose effect is especially pronounced in colloidal particles.

When electric conductivity is being measured in the high frequency field, particles oscillate so rapidly that there is no time for complete asymmetry of the double layer to develop. As a result, relaxation decreases and electric conductivity increases.

In a field of very high voltage (10^5 V/cm), the velocity of particles becomes so great that they tear away from the atmosphere of ions surrounding them. This results in the disappearance of electrophoretic retardation and electric relaxation.

Dielectric constant of lyosols. The dielectric constant of lyosols differs from that of the dispersion medium for the following reasons.

1. The dielectric constant of sol particles is usually smaller than that of the dispersion medium, so that the total dielectric constant of a sol decreases. This effect is apparently a simple volume effect.

2. Sol particles may have a permanent dipole moment. Dipoles orient when the dielectric constant in the electric field is being determined; as a result, polarization grows and the value of ε increases. This effect is usually inconsiderable for typical colloidal systems whose particles do not have a permanent dipole moment. But the effect can considerably increase the dielectric constant for solutions of compounds of high molecular weight whose molecules may have a permanent dipole moment.

3. Sol particles may acquire dipole moments whose direction is opposite to that of the external electric field owing to the deformation of the electric double layer in the field. Apparently, the centres of gravity of the positive and negative charges of particles are displaced relative to one another, i.e., the particles are polarized, and this causes the dielectric constant to grow. Such an effect is characteristic of all colloidal systems and solutions of electrolytes of high molecular weight.

4. Sol particles can be hydrated or, in general, solvated. The molecules of a medium in the solvate layer are adsorbed and oriented under the action of considerable adsorption forces, which causes a decrease in polarization and, consequently, in the dielectric constant of a system.

The dielectric constant must be measured by means of alternating current because of the electric conductivity of lyosols; the values obtained depend on the frequency of the current. When frequencies

are not too high, the value of the dielectric constant does not considerably differ from the values which could be found in the static field because particles are completely polarized in a length of time that is smaller than the duration of a single oscillation of the field. But when frequencies are high, the last requirement is no longer met and there is a dispersion of the dielectric permittivity in a solution; the nature of this dispersion depends on the factor that determines its specific features for a given system.

In the first case, when the deviation of the dielectric permittivity is caused by a simple volume effect, and its dispersity is not observed. In the second case, dispersion occurs at a frequency when dipoles can no longer follow the change in the field direction. In the third case, dispersion is observed at a frequency which no longer causes the asymmetry of the double layer, i.e., at a frequency which corresponds to an increase in electric conductivity. It is still not clear whether particle solvation affects dispersion. Available experimental data show that the dielectric constant of solutions of gelatine and agar increases with frequency; this may be interpreted not only in terms of a change in the hydration of macromolecules, but also by the action of several other factors: the effect of frequency on the double layer, on the behaviour of permanent dipoles, and so forth.

8

OBTAINING AND PURIFYING COLLOIDAL SYSTEMS. STRUCTURE OF COLLOIDAL MICELLES

By the size of particles of a dispersed phase, sols hold an intermediate place between true solutions and suspensions; therefore, they can be obtained either by the combination of molecules or ions of a solute into aggregates, or by dispersing large particles. In conformity with this, Svedberg divides the methods of obtaining colloidal systems into *condensation* and *dispersion* ones. There is also the *peptization* method which consists in transforming precipitates whose primary particles already have colloidal dimensions into colloidal solutions. Moreover, colloidal systems can sometimes be formed by the *spontaneous dispersion* of the dispersed phase in a dispersion medium.

The two main requirements for obtaining colloidal systems, regardless of the preparation methods used, are the insolubility or low solubility of the dispersed phase in a dispersion medium and the presence of substances that are capable of either stabilizing particles which are formed in the system, or, when condensation methods are used, retarding their growth. Such substances may be both extraneous substances which are introduced into a system, and compounds which are formed when the dispersed phase reacts with the dispersion medium.

1. METHODS OF OBTAINING COLLOIDAL SYSTEMS

Condensation method. It is usually assumed that the formation of colloidal systems as a result of condensation is nothing but crystallization, and the particles formed are minute crystals. Such views were held, for example, by the Russian scientist P. Weimarn, one of the first researchers who thoroughly studied the condensation methods of forming lyosols.

Normal crystals are formed in two stages:

(1) the nucleation (origination of crystallization centres) in a supersaturated solution; supersaturation may be brought about by a chemical reaction yielding a slightly soluble compound, by a decrease in the solubility of a compound when one solvent is replaced with another, by the cooling of a solution, and other causes;

(2) the growth of nuclei, leading to the formation of sufficiently large crystals.

It was assumed for a long time that nucleation occurs spontaneously. Such a viewpoint was evolved by G. Tammann. He believed that, in some regions of a supersaturated solution which is in a metastable state, molecules or ions of a solute can arrange themselves in a crystalline order without the participation of suspended extraneous particles and form minute nuclei which are capable of growing further.

According to that viewpoint, the nucleation rate u_1 is proportional to relative supersaturation and can be expressed by the equation

$$u_1 = k \frac{c_{sup} - c_s}{c_s} \tag{8.1}$$

where k = proportionality factor;
c_{sup} = concentration of a supersaturated solution;
c_s = concentration of a saturated solution (normal solubility of a substance).

The difference of $(c_{sup} - c_s)$ represents an excess of a substance which is capable of forming crystals and consequently can serve as a measure of the rate of liberation of a substance from a solution. The quantity c_s characterizes the interaction between a solute and a solvent, and is thus a measure of resistance to the liberation of a substance from a solution. It is believed that the greater the difference of $(c_{sup} - c_s)$ and the smaller the quantity c_s, the more rapidly are the nuclei formed, the larger is the number of crystallization centres, and the smaller are colloidal particles, because the liberated substance will be distributed between a larger number of crystallization centres.

However, it was experimentally found that the nuclei of crystallization are formed as a rule not by a successful collision of molecules or ions in a solution owing to the fluctuations of concentration, but as a result of the deposition of a solute on minute extraneous dust particles which accidentally got into a system. For example, crystals are not formed for a long time in solutions which are thoroughly purified in order to remove extraneous suspended particles, even when these solutions are considerably supersaturated. Crystallization begins instantaneously in such solutions when extraneous nuclei or crystals of a solute are introduced into them. It was thus

believed that nuclei (crystallization centres) could appear at the already formed interfaces.

The theory of the formation of a new dispersed phase originated in the investigations of the thermodynamics of surface phenomena carried out by Gibbs (1878), and was evolved in the 1920's by M. Volmer and others in the experimental and theoretical investigations of the condensation of supersaturated vapour. Volmer's views on nucleation in supersaturated vapour are considered in detail in Chap. 11 which is on aerosols. Let us only indicate that the solubility or pressure of saturated vapour of small particles of any phase is, on a purely thermodynamic basis, higher than that of large ones (W. Thomson's rule). In other words, an increase in the dispersity of a phase increases its solubility in the surrounding medium or the ability of a substance to liberate from a given phase. Therefore, a solution saturated relative to large crystals is still unsaturated relative to small ones of the same substance. Under such conditions, it is hardly probable for sufficiently large crystal nuclei to be formed spontaneously whereas very small nuclei originating by fluctuations cannot cause crystallization because a solution is not supersaturated relative to them. The nuclei of a new phase may apparently be formed only at very high degrees of supersaturation when it is statistically more probable for comparatively large nuclei to originate.

The foregoing can be explained also in a somewhat different way. The formation of microcrystalline colloidal particles is a transition of a metastable phase* to a stable one, and is accompanied with a decrease in the free energy of a system. This is a spontaneous process with the exception of the nucleation stage. A sufficient number of nuclei must be formed before transition of a metastable phase to a stable one. However, for a large number of nuclei to originate, energy must be spent on the creation of a new interface between the stable and metastable phases. Since the transition of a metastable phase to a stable one at the first nucleation stage is always accompanied with an increase, rather than a decrease, in free energy owing to the formation of a new surface, it cannot occur spontaneously until the nuclei formed in a system attain a definite size. The transition is then spontaneous.

The matter is quite different if a system has extraneous nuclei or if crystals of a stable phase obtained separately are introduced

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* The metastable state in thermodynamics is a state of a system which does not correspond to stable equilibrium under given conditions but is preserved in time. Such, for example, is the state of a supersaturated vapour or solution, a supercooled or a superheated liquid, or an unstable crystalline modification. The metastable state can change to a stable one under the action of weak external effects or upon an introduction of nuclei of a more stable phase into a system.

into it. Then, a new phase is formed more easily because a system has an interface at which condensation processes readily occur.

The introduction of extraneous nuclei is the basis for obtaining sols with preset dispersity because any number of extraneous nuclei may be introduced into a supersaturated solution, and the substance which forms a crystalline phase is distributed among them. This will be dealt with in greater detail when the methods of synthesizing colloidal systems are discussed.

It follows from the foregoing that the application of Eq. (8.1) is confined to a very narrow range. Nevertheless, it indicates the way of regulating dispersity when a colloidal system is being formed. To increase dispersity, it is necessary, according to Eq. (8.1), to increase relative supersaturation, i.e., either to increase c_{sup} or reduce c_s, or simultaneously increase c_{sup} and reduce c_s.

Let us consider the second stage of the formation of a colloidal system: the growth of nuclei of crystallization as a result of the deposition of a substance from a supersaturated solution on them. Many theories were proposed to explain crystal growth.

In interpreting phenomena connected with crystal growth, J. Gibbs, J. Currie, and later the Russian scientist G. Wulff proceeded from the connection between the shape of a crystal and the surface energy of all its faces. According to diffusion theories, the formation of a crystal face occurs at an infinitely high rate and therefore depends only on the rate at which a substance is supplied to a crystal from a solution, i.e., on the diffusion rate. In the 1920's, Volmer proposed the adsorption theory in order to explain crystal growth; according to the theory, the particles of a substance being crystallized form, as they attain the surface, a peculiar adsorption layer, i.e., a two-dimensional crystalline formation which then links up to a crystal face. I. Stranski believes that ion rows or layers similar to Volmer's two-dimensional crystalline formations may originate on a growing crystal.

If the diffusion mechanism of crystal growth is accepted, the rate of this growth u_2 may be represented by the equation

$$u_2 = \frac{Ds}{\delta}(c_{sup} - c_s) \tag{8.2}$$

where D = diffusion coefficient;
s = crystal surface area;
δ = thickness of the solution layer through which diffusion occurs (in this layer, the concentration of a substance grows from c_s on the surface to c_{sup} in the volume of a supersaturated solution).

As a result of nucleation, a solution becomes less saturated due to the transition of a solute to a crystalline phase and, at the same

time, particles become less soluble as their dimensions increase. Only as the first approximation does Eq. (8.2) describe crystal growth, and by no means under all conditions. The connection between the growth rate and the extent of supersaturation is often complicated, and many details of the process are still not clear. For example, there are grounds to assume that the rate of crystal growth sometimes is determined not by diffusion but by the rate at which molecules of a substance are deposited on crystal faces. Only the growth of large crystals having well-formed faces has been studied relatively well. In the formation of minute colloidal particles, only the initial stages of growth are important.

When a colloidal system is being obtained, the nucleation rate u_1 must be high and the crystal growth rate u_2 must be low because only then are many crystals formed and each of them has colloidal dimensions. Conversely, if the rate u_1 is low and the rate u_2 is high, the substance will be deposited on a small number of nuclei and, consequently, a small amount of large crystals will be formed. Monodispersed sols will be formed in the first case, and polydispersed ones in the second case. Indeed, a small number of nuclei originates at the beginning of sol formation when the nucleation rate is low and the rate of nuclei growth is high; at the end of this formation, the nuclei grow to large crystals while the crystals formed on nuclei which originated at the end of the process remain small.

The concentration of reacting solutions is important in obtaining colloidal systems. As a result of chemical reactions yielding slightly soluble substances, sols are obtained when the concentrations of reactants are low, precipitates when concentrations are high, and gels when concentrations are very high. This may be clearly traced by taking the example of the reaction between potassium ferrocyanide, $K_4[Fe(CN)_6]$, and ferric chloride, $FeCl_3$, yielding Berlin blue, $Fe_4[Fe(CN)_6]_3$. If concentrated solutions of ferric chloride and potassium ferrocyanide are rapidly mixed together in equivalent amounts, Berlin blue will separate as a thick gel. A small amount of this gel produces a stable sol when it is stirred in a large volume of water. If solutions diluted ten-fold are taken instead of concentrated solutions of initial substances, a precipitate will be formed which cannot be converted to a sol no matter how much it is stirred. A stable sol of Berlin blue will be obtained if the solutions of ferric chloride and potassium ferrocyanide are diluted to a very great extent and then mixed.

Let us now explain all these phenomena. The crystallization rate is not high in greatly diluted solutions because, for a crystal to grow, a solute must at first diffuse to them. In these cases, a sufficiently large number of nuclei is formed during the time needed for the transition of the substance to a crystalline phase. In very concentrated solutions, the nucleation rate is high because crystallization can-

not lead to the rapid utilization of a large amount of a substance, and stop nucleation. In solutions of intermediate concentration, the nu-cleation and crystallization rates are approximately the same, and relatively large particles are formed.

By introducing into a system during the formation of a colloidal solution various specially selected substances which hinder nucleation or inhibit growth of nuclei, Hige as early as 1914 studied separately the role of the rate of formation of crystallization centres and that of the rate of growth of microcrystals. Substances which prevent or inhibit nucleation are $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$, and substances which retard crystal growth are KBr and KI. When the former two substances are introduced, crystals are not formed from the supersaturated solution, but crystallization may be easily caused if extraneous nuclei are added into a system. Sols having minute, submicroscopic particles may be obtained by adding substances which inhibit growth of crystals.

The action of substances which prevent nucleation is probably due to purely chemical phenomena which occur in a solution. The action of substances which inhibit the growth of nuclei is caused by their adsorption on incipient crystals and the formation, on the crystal surface, of a very thin foreign layer which prevents the further growth of a crystal. This is confirmed by the fact that the dependence of the rate of crystal growth on the equilibrium concentration of a substance which hinders growth can be expressed by an equation which resembles Freundlich's adsorption equation.

The rate of growth of crystal faces can be changed differently by special additives. For example, the shape of the AgI crystals changes when methyl violet is introduced as the silver iodide sol is being obtained. This is apparently due to the fact that the molecules of methyl violet are adsorbed preferably on crystal faces having the greatest surface energy, and this retards crystal growth in a direction perpendicular to a given face.

Besides the theory which considers the formation of colloidal systems as crystallization, it was believed that colloidal systems having amorphous particles which only later assume a crystalline structure may be obtained when a substance precipitates rapidly from a solution. For example, Haber as early as 1922 assumed that the nature of a new phase depended on the rate of two processes: the rate of ordering and the rate of aggregating of molecules. If the rate of the first process is higher, crystalline particles may be obtained, and if the second process occurs more rapidly, an amorphous phase originates. Dumansky was of a similar opinion.

V. Kargin and Z. Berestneva have shown that the formation of amorphous particles in the production of colloidal systems is a rule rather than an exception. They observed the formation of particles by means of an electron microscope and found that round or

shapeless, amorphous particles appear at first when the sols of titanium dioxide, silicon dioxide, arsenic sulphide, aluminium hydroxide, vanadium and gold pentoxides are being obtained. Fig. 8.1*a* gives an electron micrograph of particles of a freshly-obtained sol of titanium dioxide; the particles are 0.1-0.8 μm large and aggregate in chains. The amorphism of these particles can be seen from Fig. 8.2*a* which is an electron-diffraction pattern of the same preparation.

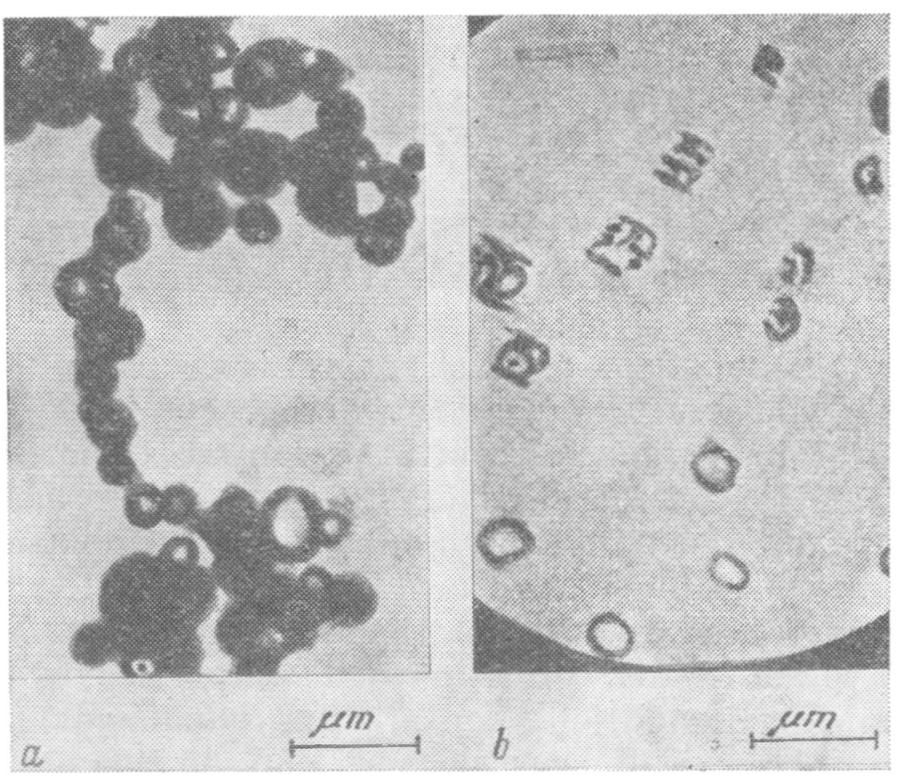

Fig. 8.1. Electron micrographs of particles of a titanium dioxide sol:
a—freshly prepared sol; *b*—sol 1-2 hours after preparation

However, some time after the formation of these sols, ordering and crystallization occur inside particles which disintegrate then into crystals. Fig. 8.1*b* gives, as an example, an electron micrograph of a preparation of an aged titanium dioxide sol; many minute crystalline formations are seen now within the initial amorphous spheroidal particles. Rings of point reflexes simultaneously appear on electron-diffraction patterns (Fig. 8.2*b*) which confirm the crystalline structure of the minute particles formed.

The lifetime of amorphous particles is very different for various colloidal systems. For example, the particles of a gold sol crystallize 3-5 minutes after its preparation; a vanadium pentoxide sol, after one hour; a titanium dioxide sol, after 1-2 hours; an aluminium hydroxide sol, after one day; and a silicic acid sol, after two years. The crystallization rate seems to be determined by the rate of formation of ordered regions and their number.

Temperature strongly affects the rate of crystallization of the initially formed amorphous particles. For example, the particles of the sols of aluminium hydroxide and titanium dioxide, prepared at 80-90 °C, immediately give electron-diffraction patterns that are characteristic of fine crystals. Crystallization at elevated temperatures in these sols apparently occurs so rapidly that it is hardly possible to obtain an electron-diffraction pattern of the amorphous particles being initially formed.

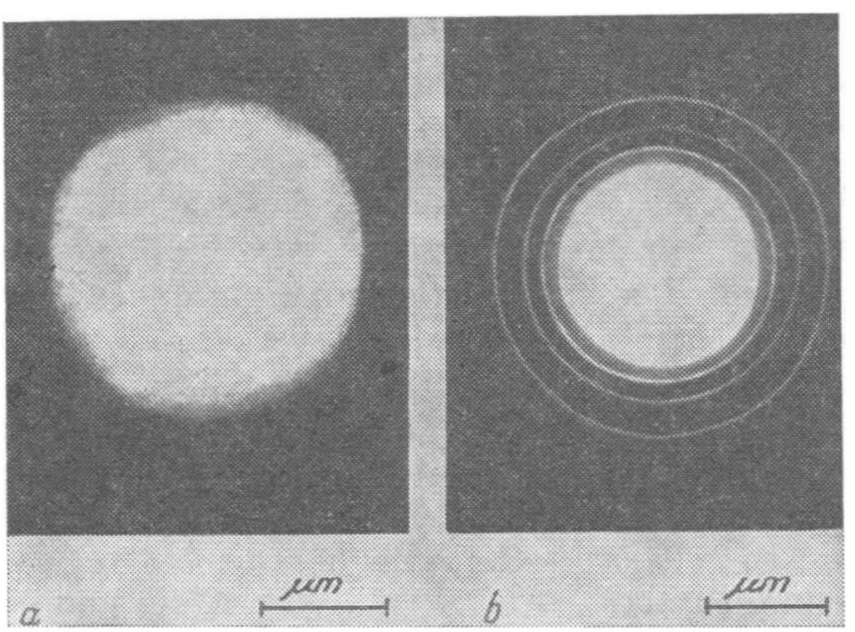

Fig. 8.2. Electron-diffraction patterns of particles of a titanium dioxide sol: *a*—freshly prepared sol; *b*—sol 1-2 hours after preparation

The further aging of these colloidal systems is accompanied with both the crystallization of particles and their aggregation, often as chains or reticular structures, which indicates the heterogeneity of colloidal particles. But even primary spherical amorphous particles form chains, suggesting that they also have on their surface more active regions in which their sticking together occurs.

V. Kargin and Z. Berestneva believe, on the basis of the experimental data, that the crystallization in solutions as the primary act of formation of colloidal systems is hardly probable. It is difficult to assume that, when molecules, atoms, or ions collide with one another, they immediately combine in an order which corresponds to their crystal lattice, especially since colloidal systems are obtained from supersaturated solutions. A more probable fact is that every collision causes the sticking together of particles in a supersaturated solution. Since collisions between molecules, atoms, or ions are equally probable in all directions, the primary particles of a new phase usually have a spherical shape and an amorphous structure. The colloidal particles formed differ in dispersity, apparently owing to the same factors which cause the diverse rates of

growth of crystal planes in the presence of impurities that may either accelerate or decelerate growth.

Owing to the capture of molecules of a dispersion medium by loose amorphous particles being formed, molecules, atoms, or ions within an amorphous particle remain sufficiently mobile. Since the system formed is not in equilibrium, particles crystallize, and this causes the free energy of a system to diminish. Origination of crystalline formations within an amorphous particle creates stresses in it, and the particle disintegrates into many small crystals. Thus, the dimensions of these crystalline particles depend not on the conditions of their growth from a solution, as was supposed earlier, but on crystallization as the primary amorphous particles disintegrate. It is probable that the given mechanism of the formation of a new crystalline phase in colloidal systems is widespread.

This mechanism was confirmed by M. Talina who studied the formation of ferric hydroxide sols from ammonium carbonate and iron chloride by Graham's method. However, the particles of ferric hydroxide sol obtained by hydrolysis had an amorphous structure as was shown by electron microscopy and X-ray analysis.

Hence, sol particles may be formed according to various mechanisms.

In the above-mentioned theories of the formation of colloidal systems by condensation, the appearance of sufficiently small particles was regarded as the main prerequisite of the sedimentation stability of a colloidal system. But this is not enough for obtaining colloidal system which exists for a long time; aggregative stability is also required. N. Peskov indicated that, in order to obtain a sol, it is not enough to disintegrate the dispersed phase in a dispersion medium to particles having colloidal dimensions.

The aggregative stability of colloidal systems is determined by the charge of the same sign of colloidal particles as a result of selective adsorption, on their surface, of one of the ions of a stabilizing electrolyte present in a system. There are also several other explanations of aggregative stability of hydrophobic colloidal systems. However, they all envisage the adsorption of a stabilizer present in a system on the surface of particles, and this determines the interaction between the dispersed phase and the dispersion medium which is inert to the phase. The stabilization of colloidal particles is considered at greater length later in the section of this chapter that is on the structure of micelles of various sols, and in Chap. 9.

A variety of the condensation method is polymerization which is used to obtain synthetic latexes; these latexes are aqueous dispersions of polymers, i.e., typical colloidal systems. However, we will not consider the mechanism of obtaining synthetic latexes here; it is elucidated in the textbooks of chemistry and physics of polymers.

Dispersion method. Before dealing with the technique of obtaining colloidal systems by dispersing coarse particles, let us consider, at least briefly, the dispersion process in general.

Dispersion is a term applied to disintegration of solids or liquids in an inert medium (a medium which does not react with the substance being disintegrated) when dispersity sharply increases and a system having a considerable specific interface area is formed. In contrast to dissolution, dispersion as a rule occurs not spontaneously, but with an expenditure of external work done in overcoming intermolecular forces when a substance is being disintegrated.

Dispersion is used in several types of technological processes: the production of highly dispersed powders which are active fillers for polymers and pigments for dyes; the preparation of a graphite suspension for lubricants; the grinding of mineral ores before their concentration; the preparation of flour and other foodstuffs, and so forth.

A study of the mechanism of dispersion of solids has shown that microcracks are formed on the surface of a solid when it is being deformed. A. Ioffe and his school have shown that it is precisely the formation of microcracks and especially surface microcracks which is the main cause of the reduced strength of solids in comparison with the theoretical strength calculated by the data on their structure.

Microcracks are usually formed in weak places of a crystal lattice. All solids have structural defects that are distributed in such a way that the regions of a solid between them have dimensions averaging 10^{-6} cm. In other words, one defect is found on the average after 100 regular intermolecular or interatomic distances. The "weak sites" may be both the boundaries between crystals, provided a body consists of microcrystals, or any heterogeneous regions. When the load is removed and the body has not been disintegrated, the microcracks disappear or "heal", according to Rehbinder. When the loads are greater than the factor of safety, a body disintegrates mainly along these microcracks.

P. Rehbinder, Ye. Shchukin and others have shown that microcracks may develop, under the action of external deforming forces, much faster when various substances are adsorbed from a medium in which dispersion is being conducted. Both the ions of electrolytes and the molecules of surfactants may be adsorbed, form a two-dimensional gas on the surface as a result of non-localized adsorption, penetrate under the pressure of this gas into the openings of the microcracks formed, and tend to widen each microcrack, thus assisting external deforming forces and promoting dispersion.

Fig. 8.3 schematically illustrates the development of microcracks under the action of a two-dimensional gas which is formed as a result of the adsorption of a substance on the surface of a particle. Dis-

persion is facilitated not only by the pressure of the gas, but also by the screening of the cohesive forces which operate between the opposite surfaces of a crack when a substance gets into the microcracks being formed.

The facilitation of dispersion by adsorption is known as the *Rehbinder effect* or the *adsorptive reduction of hardness*, and substances which increase the effectiveness of dispersion are known the *reducers of hardness.*

The adsorptive reduction of hardness is used not only in obtaining dispersed systems, bus also in roughly disintegrating and deforming various materials, such as in boring rocks, treating metals on metal-cutting machine-tools, and so forth. Owing to the adsorptive reduction of hardness, these processes are accelerated, energy expenditures are reduced, and the cutting tool has a longer service life.

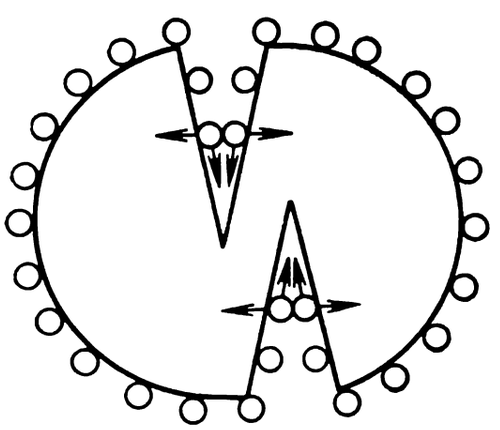

Fig. 8.3. Diagram of the development of microcracks under the pressure of a two-dimensional gas

In the obtainment of colloidal systems by dispersion, powders whose particle dimensions are over several micrometres are usually formed in simple mechanical crushing or grinding. This limit of dimensions is determined by the fact that particles also stick together in mechanical grinding. However, P. Weimarn noticed as early as 1912 that the dispersity of a product increases considerably if sugar or other organic compounds are added to insoluble oxides, sulphides, or chlorides of metals which are ground in a mortar. Similar results were obtained in Svedberg's laboratory. Stable suspensions of sulphur were formed when sulphur was ground with urea, and the mixture obtained was dissolved in water. Such an action of the third component is due to the adsorptive reduction of hardness. Moreover, the substance which promotes dispersion may be a stabilizer.

Nevertheless, dispersion methods are usually inferior to condensation methods with respect to the dispersity of the systems obtained. Systems whose particle dimensions are below 1μm are obtained rarely by dispersion even in the presence of a stabilizer.

Peptization method. *Peptization* is a term applied to the passage into colloidal solution of precipitates formed in coagulation. The term was introduced by T. Graham on the basis of an apparent similarity of the peptization method with the dissolution of proteins under the action of pepsin. Peptization may occur when a precipitate is washed, or it may be caused by the action of special substances,

peptizers (peptizing ions). Coagulating ions are removed from the precipitate or peptizing ions are adsorbed by the colloidal particles of the precipitate; this causes the formation of electric double layers or solvate shells around colloidal particles which counteract the cohesion between particles. Free particles are now distributed, under the action of thermal motion, throughout the liquid volume. Hence, peptization is opposite, as it were, to coagulation.

A precipitate cannot always be peptized. Peptization is hindered by recrystallization and aging, which cause the particles to stick together. Moreover, it is difficult to peptize a precipitate obtained by coagulating a sol with polyvalent ions which are firmly bound to the surface of the particles that have adsorbed them.

In peptization, as in coagulation, stoichiometric ratios are not observed between the amount of peptizing ions and that of a peptized precipitate. To peptize a precipitate and obtain a lyosol, it is not necessary for the surface of particles to be covered with a layer of adsorbed peptizing ions. For example, Fajans found that, in order to obtain a stable sol of silver bromide, only 1/4-1/10 of the surface area of particles must be covered with peptizing ions, in this case, bromide ions. However, the dispersity of particles in the sol depends on the amount of peptizing ions. When the content of peptizing ions is low, particles of higher orders that consist of several primary particles are formed, and when it is large, primary particles are formed.

Peptization occurs at a definite rate; when there is a sufficient amount of a peptizer, the process occurs at first very rapidly, and then gradually slows down. Of course, the stirring of a system promotes peptization. When stirring is good, the penetration of a peptizer into aggregates is accelerated, and this helps particles to tear away from one another and pass into solution. The peptization rate increases with temperature.

In peptization, a characteristic relationship is observed among the amounts of a peptized substance, of the precipitate taken, and of the peptizer. This relationship which is sometimes known as the precipitate rule and has been studied by W. Ostwald and Buzag consists in the following. When the content of a peptizer is constant and as the amount of the precipitate taken for peptization grows, the amount of the precipitate which has passed into solution first increases and then decreases (Fig. 8.4).

Let us explain the precipitate rule. A minimum amount of a peptizer is needed for peptizing a particle of a precipitate. Therefore, in introducing the first portions of a precipitate when a system has a large amount of a peptizer and a small amount of a precipitate, the latter readily passes into sol. However, as the precipitate is added further, the amount of the peptizer per particle of the precipitate will diminish. This will at first cause a decrease in colloidal dissolution. Afterwards, when the amount of a substance being

peptized becomes large in a system, the precipitate will no longer dissolve and even its amount that has dissolved will precipitate because, owing to the redistribution of the peptizer between colloidal particles, its amount will no longer be enough for these particles to remain in the solution.

As it follows from the relationship between the amount of a colloidally dissolved precipitate and the amount of a precipitate taken for dissolution, peptization greatly differs from ordinary dissolution.

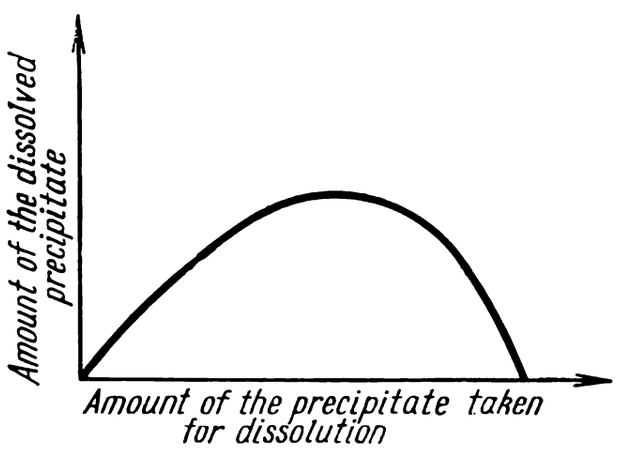

Fig. 8.4. Dependence of the amount of the dissolved precipitate on the amount of the precipitate taken for dissolution (when the content of the peptizing electrolyte is constant)

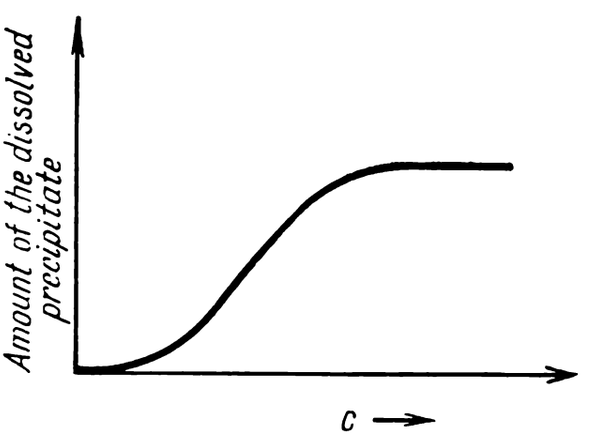

Fig. 8.5. Dependence of the amount of the dissolved precipitate on the concentration *c* of the peptizing electrolyte (when the amount of the precipitate taken for dissolution is constant)

In the latter process, the content of a solute no longer depends on the amount of a substance taken for dissolution after saturation is attained. This difference is due to the fact that a peptizer is needed for colloidal dissolution whereas a third component is not needed for true dissolution.

If the same amounts of a precipitate are taken for dissolution and they are peptized by different, ever increasing amounts of a peptizer, peptization will rapidly develop until the precipitate will be completely peptized (Fig. 8.5). Such a dependence can also be explained by the fact that a definite amount of a peptizer is needed for the colloidal dissolution of a precipitate.

Peptization is of great importance in a technological process when various precipitates are being converted into colloidal solutions, and in preparative colloid chemistry when sols are being obtained. But peptization may also often act negatively. For example, when sugar is being extracted from beet by diffusion, pectin and other substances contained in plant tissues may be peptized.

Spontaneous dispersion. The spontaneous formation of equilibrium and stable colloidal systems is an interesting phenomenon. In some

cases, a solid or a liquid may be spontaneously dispersed in a liquid medium with the formation of a two-phase, though thermodynamically stable, colloidal or microheterogeneous system. As we have already seen in Chap. 1, Rehbinder proposes to call such systems obtained by spontaneous dispersion *lyophilic* colloidal systems because of the rather strong interaction between the substance of a dispersed phase and the medium.

Such systems include critical emulsions which originate spontaneously at temperatures close to critical ones, highly dispersed sols

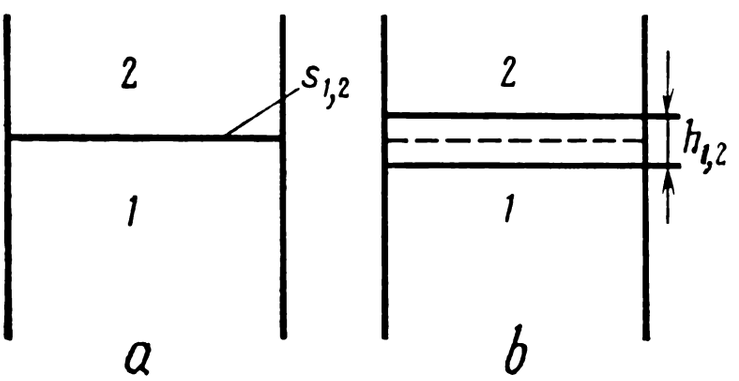

Fig. 8.6. Interface:
a—of an ideal system; *b*—of a real system.
$s_{1,2}$—interface; $h_{1,2}$—total thickness of the boundary interfacial layer which is equal to the sum of thickness h_1 and thickness h_2 of the layers of the first and second phases near the interface

of paraffin in hydrocarbons, and aqueous solutions of Emulsols, i.e., hydrocarbons having a large content (10-40 per cent) of soaps or soap-like surfactants (Emulsols are used as coolant-lubricants in the cold working of metals). These systems may exist for a long time without any noticeable changes.

A lively discussion was held (by P. Rehbinder, G. Fuchs, E. Shchukin, and others) on the causes of the origination and existence of such systems; so far, it did not lead to the final solution of the question. However, taking into account the fundamental importance of the spontaneous origination of thermodynamically equilibrated two-phase systems, this process should be considered in greater detail on the basis of the concepts evolved by Rehbinder.

Classical lyophobic systems, and lyophilic systems in the new sense of the word, are characterized by an interface which divides phases 1 and 2 (Fig. 8.6*a*). However, the interface is actually not a geometric plane, but has a certain thickness $h_{1,2}$ although it is very small owing to a sharp decrease in the action of molecular forces with distance (see Fig. 8.6*b*). In this case, it would be proper to speak of a boundary interfacial layer.

The free energy F of a system including the interfacial layer may be expressed by the equation

$$F = F_1 + F_2 + F_{1,2} = f_1 V_1 + f_2 V_2 + \sigma_{1,2} s_{1,2} \qquad (8.3)$$

where F_1 and F_2 = free energies of the first and second phases;
f_1 and f_2 = densities of the free energy of these phases;
V_1 and V_2 = phase volumes;
$F_{1,2}$ = free energy of the boundary interfacial layer;
$\sigma_{1,2}$ = condensation of free energy in the boundary interfacial layer having an area of $s_{1,2}$.

In the phase volume, the densities of energies f_1 and f_2 are constant. However, energy density near the interface increases closer to the interface due to the energy of interaction between phases or owing to the non-compensation of intermolecular forces in the interfacial

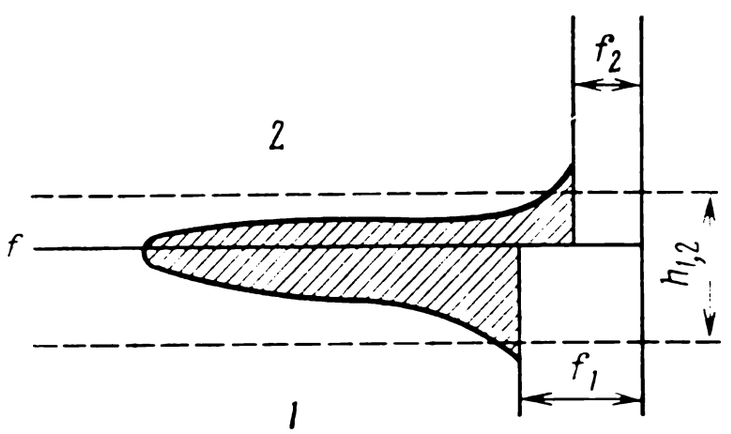

Fig. 8.7. Change in the density of free energy f at the interface of lyophobic colloidal systems

layer. Thus, a transition from the energy level f_1 of the first phase to the energy level f_2 of the second phase is effected through an energy barrier which corresponds to the condensation of free energy in the interfacial layer. This layer is shown as a crosshatched "tongue" in Fig. 8.7. The area of the "tongue" corresponds to the condensation of free energy in the interfacial layer or, for a layer having an area of one square centimetre, to interfacial tension $\sigma_{1,2}$.

In typical lyophobic colloidal systems, the interfacial layer is characterized by a great increase in the density of free energy and by a distinct interface. In this case, $\sigma_{1,2} \gg \sigma_{cr}$, where σ_{cr} is the critical value of interfacial tension at which a thermodynamically equilibrated colloidal system may be formed, i.e., spontaneous dispersion occurs as a result of the thermal motion of a substance. Therefore, in lyophobic systems (at $\sigma_{1,2} \gg \sigma_{cr}$) spontaneous processes may only be coagulation, structuralization, recrystallization, and so forth.

In lyophilic colloidal systems, the interfacial layer is characterized by a small increase in the density of free energy and does not have a distinct interface. Fig. 8.8 shows a diagram which characterizes the condensation of energy in the interfacial layer of particles of a lyophilic sol. The difference $(f_1 - f_2)$ here is very small and the energy barrier in this case is almost absent. Therefore, lyophilic

systems (in the new sense of the word) are capable of undergoing spontaneous dispersion under the action of thermal motion.

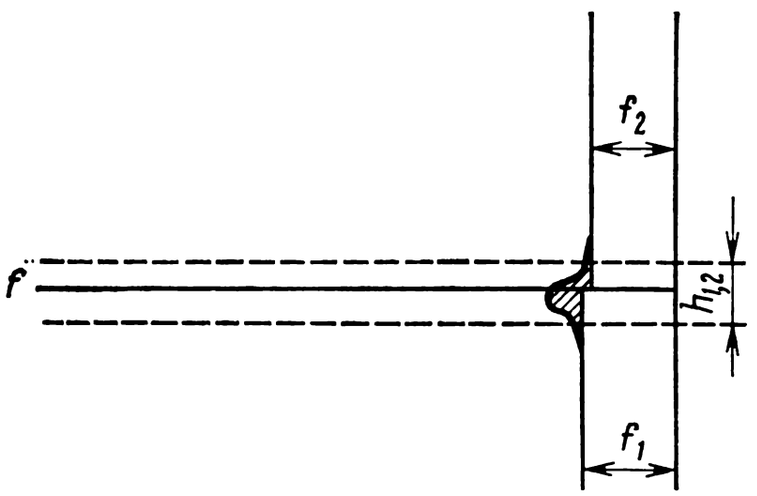

Fig. 8.8. Change in the density of free energy f at the interface of lyophilic colloidal systems

The change in free energy ΔF in spontaneous dispersion may be represented by the equation

$$\Delta F = \Delta U + \Delta s_{1,2}\sigma_{1,2} - T\Delta S \tag{8.4}$$

where U = internal energy;
S = entropy.

In this case, ΔU is close to zero. The condition of spontaneous dispersion will then apparently be expressed by the inequality

$$\Delta s_{1,2}\sigma_{1,2} - T\Delta S \leqslant 0 \tag{8.5}$$

The first term of the left-hand member of this inequality represents a growth of free energy in dispersion, and the second term characterizes a reduction of free energy owing to the uniform distribution of the dispersed phase in volume. When the quantity $\sigma_{1,2}$ is sufficiently small, the entropy term may prevail as a result of which autodispersion occurs.

From Eq. (8.5), we may obtain

$$na^2\sigma_{1,2} \leqslant n\gamma kT \tag{8.6}$$

where n = number of particles;
a = size of particles;
k = Boltzmann constant;
γ = dimensionless coefficient.

The quantity na^2 is proportional to the change in surface, and the quantity $n\gamma k$, to the change in the entropy of a system in dispersion. The constant γ in dispersion to particles of colloidal dimensions has the value of about 10.

From Eq. (8.6), we may obtain the critical value of surface tension

$$\sigma_{cr} = \frac{\gamma kT}{a^2} \tag{8.7}$$

For particles of colloidal dimensions, $a \approx 10^{-6}$ cm, and $\sigma_{cr} \approx$ ≈ 0.01 erg/cm^2. In other words, spontaneous dispersion can be used to obtain colloidal systems for which $\sigma_{1,2} < \sigma_{cr} \approx 0.01$ erg/cm^2.

In spontaneous dispersion, dispersed systems are formed that have normal distribution curves with a certain, most probable, radius of particles. This means that there is optimum dispersity which is characteristic of a given system. Rehbinder and his coworkers believe that further spontaneous dispersion to molecules is impossible. According to them, the thermodynamic stability of two-phase dispersed systems is determined by two conditions: sufficiently low interfacial tension and its rapid increase as the radius of particles decreases. However, it is difficult to explain why interfacial tension increases as the dimensions of particles decrease.

We may give other explanations why spontaneous dispersion does not yield molecules. For example, when Emulsols are diluted with water, individual hydrocarbon molecules cannot exist in a system because hyrocarbon is insoluble in water. For this reason, the hydrocarbon molecules stick together immediately into droplets, whereas the surfactant present in a system is adsorbed on the droplets and reduces $\sigma_{1,2}$ to values less than σ_{cr}. Thus, when an Emulsol is being dissolved, two oppositely directed processes occur simultaneously: the dissolution of an Emulsol to molecules and the coalescence of hydrocarbon molecules into droplets which adsorb a surfactant. A stable equilibrium emulsion is obtained when equilibrium is established between both processes. The dimensions of droplets of this emulsion are determined by the quantitative ratio between a hydrocarbon and a surfactant, the nature of both components, temperature, and so forth.

When critical emulsions are formed as two liquids immiscible at ordinary temperature are heated, dissolution to molecules is impossible because of two simultaneously occurring, but oppositely directed, processes. On the one hand, one of the phases is dispersed to molecules; on the other hand, the droplets of this phase coalesce as a result of which dynamic equilibrium is established and then is immediately upset as temperature changes. Of course, the state of the critical emulsion also corresponds to the minimum free energy of a system.

Let us briefly generalize the thermodynamic principles which should be borne in mind when various methods of obtaining colloidal systems are being considered.

In the dispersion method, work spent on overcoming intermolecular forces when a dispersed phase is being disintegrated is stored

up by a system as free energy at the interface. Excess free energy makes a system thermodynamically unstable. To impart aggregative stability to a system, excess free energy must be reduced by adsorption. However, free surface energy hardly can be completely eliminated by adsorption, and therefore the stability of typical colloidal systems is of a temporary nature. When a substance is being disintegrated, the entropy of a system increases, but owing to the comparatively large dimensions of particles, the stability of a colloidal solution is not noticeably affected. Only at very small interfacial tensions can an increase in entropy cause spontaneous dispersion and the formation of equilibrium colloidal systems.

In peptization, external energy is not needed to convert a precipitate into a solution because a fresh precipitate consists of primary particles which have unstably sticked together only in some places. To overcome cohesive forces, it is enough to introduce a peptizer into a system; the peptizer diffuses to the particle surface and forms an electric double layer or a solvate shell on it. In this case, the uniform distribution of free and stable particles in the volume of a liquid is caused by Brownian motion.

The method of spontaneous dispersion is similar by its nature to peptization. The work of dispersion here is inconsiderable because of the small interfacial free energy, so that thermal motion alone is enough for colloidal dissolution. The growth of the entropy of a system as a result of a more uniform distribution of the dispersed substance amply compensates for the increase in free surface energy since the interface becomes larger.

The thermodynamic conditions under which colloidal systems are obtained by condensation appear to be the most complicated ones. It may even seem that the formation of sols, for example, by a chemical reaction is spontaneous and, consequently, is accompanied with a decrease in the free energy of a system. But in the case of a chemical reaction, the free energy of a system should be compared not with that of solutions of the initial components of a reaction, but with that of a system which has a crystallized dispersed phase. Then, it becomes clear why colloidal solutions obtained by condensation are unstable.

2. STRUCTURE OF COLLOIDAL MICELLES

Having become acquainted with the structure of the electric double layer which constitutes the outer shell of a micelle and with the physico-chemical principles of obtaining colloidal systems, we may now consider the structure of colloidal micelles as a whole.

Scientists have long taken an interest in the structure of micelles in sols, and there are many opinions on this question some of which are now only of historic interest.

In studying the chemical methods of obtaining various sols, Jordis in 1902 concluded that the composition of colloidal micelles did not correspond to the substances which should be formed by the supposed reaction. He was among the first to note that the dispersed phase of a sol always contains, as an impurity, substances from which it is obtained. When these substances are removed, say by dialysis, a sol loses stability. Jordis correctly assumed that impurities were not indifferent to a colloidal system. According to him, a colloidal particle is a complex compound.

Similar views were held by the French scientist P. Duclaux. Like Jordis, he considered the presence of small amounts of initial substances in colloidal systems to be very important to the properties of these systems, and believed that these impurities were in the composition of colloidal particles. For example, Duclaux represented the composition of particles of the As_2S_3 sol, which is obtained by the reaction between As_2O_3 and H_2S and always contains small amounts of H_2S, by the formula

$$As_2S_3 \cdot nH_2S$$

By using the coefficient n in this formula, Duclaux wanted to emphasize the possibility of a wide change in the content of H_2S in a colloidal particle. He was the first to propose the term "micelle" for such a complex particle. Duclaux called a small amount of a stabilizer in a micelle an "active part"; he indicated that it was precisely this part which determined the motion of a particle in an electric field and that the behaviour of a sol when electrolytes are introduced into it was caused by the presence of that part.

Pauli expanded the concepts of Jordis and Duclaux. He likewise believed that a micelle consisted of a comparatively inert nucleus and an active part which was capable of being ionized and which he called the "ionogenic complex". Pauli considered it to be a true complex compound according to Werner's theory; therefore he expressed the structure of a micelle, e.g., of the sol of arsenic sulphide, by the formula

$$x As_2S_3 \cdot y As_2S_4H^- \cdot y H^+$$

This scheme explains both the charge on the particles of the arsenic sulphide sol and the behaviour of the sol when electrolytes are introduced into it. But the scheme does not show how the ionogenic complex and the inactive part of a micelle are bound. It also cannot explain why colloidal particles are characterized by both the total potential jump at an interface and the ζ-potential which is detected only in electrokinetic phenomena.

Together with the foregoing concepts which may be regarded as chemical hypotheses of the structure of colloidal micelles, there was another, a physical or adsorptive approach to the interpretation of the micelle structure. In 1914, F. Paneth showed that the crystals

of some water-insoluble salts particularly vigorously adsorb, from the surrounding solution, ions which form slightly soluble compounds with oppositely charged ions of a crystal surface. This phenomenon occurs because, when a slightly soluble salt is being formed, hydration energy is always less than the energy of a crystal lattice.

Fajans evolved this conception further and used it to explain the formation of colloidal systems. He believed that colloidal particles were ultramicroscopic crystals and that, for example, the AgI crystals, which are yielded by the reaction between KI, taken in an excess, and $AgNO_3$ and which are in a potassium iodide solution, tend to grow. Among the ions of K^+ and I^- which are present in a solution, only I^- can form an insoluble compound with the ions of Ag^+ on the crystal surface; therefore only iodide ion is capable of completion of a crystal. This process may continue until the iodide ion covers, on the crystal surface, all the Ag^+ ions which interact with the I^- ions owing to the opposite signs of charges.

The construction of the AgI crystal is completed also when it is in the $AgNO_3$ solution. In this case, the ion that completes the construction of the surface is Ag^+ which confers a positive charge on the crystal.

The construction of the AgI crystal by I^- and Ag^+ is finished not only because these ions form an insoluble compound on the crystal surface, but also because they are identical by their dimensions and properties with the I^- and Ag^+ ions of the crystal and, consequently, are the most suitable for the given crystal lattice. The correctness of such a viewpoint is supported by the fact that the construction of a lattice may be completed not only by the ions which are the same as the ions of a crystal, but also are isomorphous with them. For example, the construction of the AgI crystal can be completed not only by I^-, but also by Br^- or Cl^- which are isomorphous with I^-.

As a result of the finishing construction, the electric double layer is formed on a crystal surface. When the AgI crystal is in the KI solution, the potential-determining ion is I^-, and the counterion, K^+; when the crystal is in the $AgNO_3$ solution, the potential-determining ion is Ag^+, and the counterion, NO_3^-.

Both the chemical and physical theories of the micelle structure lead to the same conclusions, i.e., that the ions of a stabilizing electrolyte hinder the further growth of a crystal, impart a charge to it, and thus promote the aggregative stability of a colloidal system.

However, the chemical and the foregoing adsorption concepts are far from always applicable. For example, when aqueous emulsions of hydrocarbons are being obtained with the use of ordinary soaps as a stabilizer, an electric double layer is also formed on the surface of droplets. In this case, the potential-determining ions are anions of a fatty acid which have comparatively long hydrocarbon radicals, and the counterions are cations of an alkali metal. Of course, there

can be no complex-formation or the finishing construction of a crystal lattice here because the droplets of hydrocarbon are chemically inert and amorphous, but the hydrocarbon droplets adsorb ions containing hydrocarbon radicals.

Thus, we may conclude that the charge of a colloidal particle is always determined by the similar ions of a stabilizer which complete the construction of a crystal lattice or are preferentially adsorbed on the surface of a particle. A stabilizer can be any substance which has such ions, regardless of whether it is one of the initial substances (e.g., KI or $AgNO_3$) taken in an excess when the dispersed phase is being formed (e.g., the AgI sol), or it is introduced into a system when the latter is being obtained (soap when an emulsion is being formed).

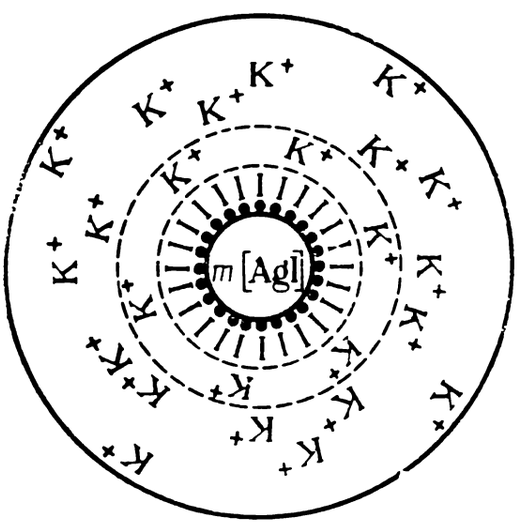

Fig. 8.9. Scheme of the micelle structure of a silver iodide sol in a weak solution of potassium iodide

Proceeding from the foregoing, the structure of micelles of various sols can be specified and expressed by special formulas.

As an example, let us take the micelle of the AgI sol in the intermicellar liquid which is a weak KI solution. Taking into account the structure of the electric double layer that is formed on the surface of a dispersed phase and using the Paneth-Fajans rule, the structure of this micelle can be represented by a scheme illustrated in Fig. 8.9. The micelle contains a crystal which consists of AgI molecules. Using the terminology proposed by Peskov, we will call this part of the micelle an aggregate because it always consists of an aggregate of atoms, molecules, or ions which form the dispersed phase. The surface of a crystal has potential-determining ions which complete its construction and impart an electric charge to it. The aggregate together with the potential-determining ions adsorbed on it constitutes the nucleus of a micelle.

A part of the counterions K^+ is in the adsorption layer, close to the nucleus; these counterions are bound so firmly by electrostatic and adsorption forces that they move together with the nucleus to the anode in the electric field. These potassium counterions together with an equivalent number of the potential-determining iodide ions can be regarded as undissociated molecules.

Henceforth, we will call the nucleus, together with the part of the counterions firmly bound with it, a colloidal particle proper.

Unlike a micelle which is electroneutral as a whole, a colloidal particle always has a charge (a negative one in this case).

The remaining counterions which are closer to the periphery of the micelle form a diffused layer of the micelle. Since Coulomb and adsorption forces weaken with distance, these ions are relatively free and move to the cathode in the electric field. The boundary between the diffused layer and a colloidal particle proper along which a micelle is "disrupted" in electrophoresis is known as the slipping surface. In Fig. 8.9, it is denoted by a dotted line.

The micelle structure may also be represented by a formula. For example, the following formula may be written for the micelle of the AgI sol whose intermicellar liquid is a weak KI solution:

$$\overbrace{\underbrace{\{m[AgI]nI^-\cdot(n-x)K^+\}}_{\text{aggregate}}xK^+}^{\text{micelle}}$$

nucleus

particle

In this formula, $m[AgI]$ is the number of AgI molecules which are contained in the aggregate of a micelle; nI^- is the number of potential-determining ions; $(n - x)\ K^+$ is the number of counterions in the immediate proximity of the nucleus; and xK^+ is the number of counterions in the diffused layer. As a rule, $m \gg n$.

Similarly, we may represent the micelle of a sol having a positively charged particle, e.g., of the sol of AgI in a weak $AgNO_3$ solution:

$$\{m[AgI]nAg^+\cdot(n-x)NO_3^-\}xNO_3^-$$

We have considered the structure of micelles whose ionogenic part is formed as a result of the adsorption of a stabilizing electrolyte which differs in chemical nature from the substance of the dispersed phase. The ionogenic part of a micelle may also be formed from a substance of the aggregate. An example of such a colloidal system is the sufficiently aged hydrosol of silicon dioxide. The aggregate surface reacts with the water surrounding it and forms metasilicic acid H_2SiO_3 which will be the stabilizer. The structure of the micelle of such a sol should be represented by the formula

$$\{m[SiO_2]nSiO_3^{2-}\cdot 2(n-x)H^+\}2xH^+$$

The numerical coefficient 2 in front of both $(n - x)$ and x in this formula is put because metasilicic acid is dibasic.

In using the schemes of the structure of micelles and their formulas, it should be borne in mind that the micelle of a lyosol is not something that is formed once and for all, but it can undergo different changes. For example, when an indifferent electrolyte is intro-

duced into a sol, the diffused part of the electric double layer contracts and, consequently, the micelle radius decreases. Then the counterions which are in the diffused layer penetrate beyond the slipping plane and, as a result, $(n - x)$ increases while x decreases. When there is a sufficient amount of an indifferent electrolyte, ions of a diffused layer may completely pass over to the adsorption layer, and the particle becomes electroneutral. For example, the micelle of the AgI sol for which the stabilizer is KI will have the formula

$$m[AgI]nI^- \cdot nK^+$$

In addition, counterions are exchanged when an indifferent electrolyte having a counterion which differs from that of a micelle is introduced. When an electrolyte one of whose ions is capable of completing the construction of a crystal lattice is introduced into a sol, the number of potential-determining ions may change. Sometimes even one potential-determining electrolyte may be replaced by another, i.e., a reversal of charge occurs, such as when an excess of $AgNO_3$ is added to the AgI sol which is stabilized by KI.

3. EXAMPLES OF OBTAINING COLLOIDAL SYSTEMS

Only the most characteristic examples of obtaining colloidal systems are given below, and mainly the essence of a technique is described because technical details can be found in special literature.

Obtaining lyosols by condensation. This method includes the obtainment of lyosols by direct condensation, by the substitution of a solvent, and by chemical reactions.

An example of direct condensation is the obtainment of a mercury sol. To this end, Nordlund passed mercury vapours through a water layer and obtained a highly dispersed emulsion of mercury in water. Sols of sulphur, selenium, and tellurium may be obtained in a similar way. By condensing, in a liquid, the vapours of copper, silver, gold, and platinum that are produced in a voltaic arc, we may obtain their sols in water, alcohols, glycerol, or benzene. The structure of micelles of these sols has been studied inconsiderably. Stabilizers in these systems are oxides of substances that are obtained when their vapours come into contact with air at high temperature. Under such conditions, the formation of oxides which possess electrolytic properties is confirmed by a noticeable growth in the electric conductivity of a system. However, sols of greater stability are obtained when stabilizing electrolytes are added to water where vapours are condensing.

If a colloidal system is obtained by solvent substitution, a substance from which a sol is to be obtained is dissolved in an appropriate solvent in the presence of a stabilizer. Then the solution is mixed with another liquid in which the substance does not dissolve. As a result, the substance separates from the solution; however, it does not precipitate owing to the presence of a stabilizer in the system, but forms a sol. This is how the hydrosols of colophony and sulphur can be obtained. J. Perrin used this method for obtaining dispersions of gamboge and mastic. The solvent of these substances is ethanol. Impurities found in inconsiderable quantities in initial substances and ethanol (oxidation products) are stabilizers. The structure of micelles of the sols thus obtained has not been studied well enough, but it is known that colloidal particles are charged negatively in all cases.

Colloidal systems can be obtained by various chemical reactions: exchange, reduction, oxidation, hydrolysis, and so forth. But colloidal systems are not always formed in reactions capable of producing sols; they are formed only at definite concentrations of the initial substances, at a definite order of their mixing and temperature, and when some other conditions are met.

A double-exchange reaction is used, for example, to obtain a silver iodide hydrosol from dilute solutions of potassium iodide and silver nitrate. When solutions containing initial substances in quantities close to equivalent ones are mixed together, a sol is not obtained, but silver iodide precipitates according to the reaction

$$AgNO_3 + KI \longrightarrow AgI\downarrow + KNO_3$$

A sol is formed if one of the initial substances is in an excess during mixing. P. Weimarn indicated the favourable role played by the excess of one of the substances participating in the formation of a colloidal system; he believed that an excess was necessary for reducing the solubility of the dispersed phase. However, it would be more correct to say that the stable AgI sol is obtained in the presence of an excess of $AgNO_3$ or KI because these electrolytes stabilize particles of silver iodide, forming an electric double layer on them.

The stability of a silver iodide sol having negatively charged particles is somewhat higher than that of the sol having positively charged ones because iodide anions are adsorbed on aggregates of silver iodide more firmly than cations of silver. As a result, the isoelectric point for the silver iodide sol corresponds to a small excess of Ag^+ ions over I^- ions.

Sols of silver bromide and silver chloride may be obtained in a similar way, but they are less stable because these compounds possess high solubility (the solubilities of the iodide, bromide, and chlo-

ride of silver in water at 20 °C are equal to 9.7×10^{-9}, 6.6×10^{-7}, and 1.25×10^{-5} mol/l respectively). The higher the solubility of the dispersed phase, the more readily do colloidal aggregates recrystallize and the more rapidly does a sol age.

Not only hydrosols can be obtained by exchange reactions. For example, a sol of silver iodide in acetone may be formed by mixing the solutions of silver nitrate and potassium iodide in acetone. This sol may also be obtained easily by dialyzing a hydrosol against acetone.

Zsigmondy's method of synthesizing gold hydrosols by reducing potassium aurate with formaldehyde shows how a colloidal system is obtained in a reduction reaction. The initial substance in this case is chlorauric acid $H[AuCl_4] \cdot 4H_2O$ which reacts with potassium carbonate in an aqueous solution to yield potassium aurate according to the equation

$$2H[AuCl_4] + 5K_2CO_3 \longrightarrow 2KAuO_2 + 5CO_2 + 8KCl + H_2O$$

The solution obtained is heated and a weak formaldehyde solution is added dropwise to it. The reduction reaction occurs according to the equation

$$2KAuO_2 + 3HCHO + K_2CO_3 \longrightarrow 2Au + 3HCOOK + KHCO_3 + H_2O$$

A red sol of gold is obtained. The stabilizer of the gold sol is potassium aurate. The structure of a micelle of this sol can be represented by the formula

$$\{m[Au]nAuO_2^- \cdot (n-x)K^+\}xK^+$$

To obtain monodispersed gold sols by this technique, an incipient gold sol (i.e., a highly dispersed sol), prepared by reducing gold chloride with phosphorus, is added to a solution before reduction. Gold which is liberated as potassium aurate is reduced in the presence of the incipient sol becomes uniformly distributed on nuclei, and this ensures the monodispersity of the end sol. All the gold liberated is deposited on nuclei, and the same number of particles as that of the nuclei introduced is formed in the sol. The dimensions of particles of such a sol are the greater, the smaller is the number of nuclei added to a solution before reduction. The technique whereby nuclei are used for obtaining monodispersed colloidal systems having particles of the desired dimensions is widely employed in colloid chemistry.

The simplest example of obtaining a sol by an oxidation reaction is the oxidation of hydrogen sulphide with oxygen in an aqueous medium. This reaction is what causes the turbidity of hydrogen sulphide water when it stands in the air. The main reaction occurs according to the equation

$$2H_2S + O_2 \longrightarrow 2S + 2H_2O$$

Oxidation reactions of greater complexity occur simultaneously, causing the formation of polythionic acids which are stabilizers of a sulphur sol. If we assume that the stabilizing electrolyte in this process is pentathionic acid $H_2S_5O_6$, the structure of the micelle of the sulphur sol can be represented by the formula

$$\{m[S]nS_5O_6^{2-} \cdot 2(n-x)H^+\}2xH^+$$

An example of obtaining a colloidal system by hydrolysis is the formation of the sols of hydroxides of heavy metals by heating or dialyzing the solutions of their salts. For example, a red-brown sol of ferric hydroxide $Fe(OH)_3$ is obtained if a small amount of ferric chloride $FeCl_3$ is added to boiling water:

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$

Boiling promotes the reaction because hydrogen chloride is eliminated with water vapours from the system. The stabilizer in this process is assumed to be iron oxychloride FeOCl which is a product of incomplete hydrolysis of ferric chloride:

$$FeCl_3 + H_2O \longrightarrow FeOCl + 2HCl$$

According to another viewpoint, the stabilizer may be ferric chloride. Hydrogen chloride can be removed from the system by dialysis as well. As a result, a sol of ferric hydroxide may be formed also when the dialysis of the ferric chloride solution is sufficiently long. According to the third viewpoint, the stabilizer may be hydrogen chloride because the surface of particles of ferric hydroxide has a large number of hydroxyl groups. These groups are capable of adsorbing the hydrogen ions that are always present in a system when a sol is being formed.

Thus, the structure of a micelle of the $Fe(OH)_3$ sol can be expressed by the following formulas depending on which substance acts as a stabilizer:

$$\{m[Fe(OH)_3]nFeO^+ \cdot (n-x)Cl^-\}xCl^-$$

or

$$\{m[Fe(OH)_3]nFe^{3+} \cdot 3(n-x)Cl^-\}3xCl^-$$

or

$$\{m[Fe(OH)_3]nH^+ \cdot (n-x)Cl^-\}xCl^-$$

Lyosols are obtained always in a more stable state if indifferent electrolytes which cause astabilization are not formed in the course of a reaction. In this respect, such reactions as

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

or

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

are more favourable for obtaining stable colloidal systems than, for example, the reaction

$$AgNO_3 + KI \longrightarrow AgI + KNO_3$$

Obtainment of sols by dispersion. This method includes the obtainment of colloidal or microheterogeneous systems by ordinary mechanical dispersion and vibration grinding, say, by ultrasonic vibrations. Electrosputtering can be related to this method although it is a combination of dispersion and condensation.

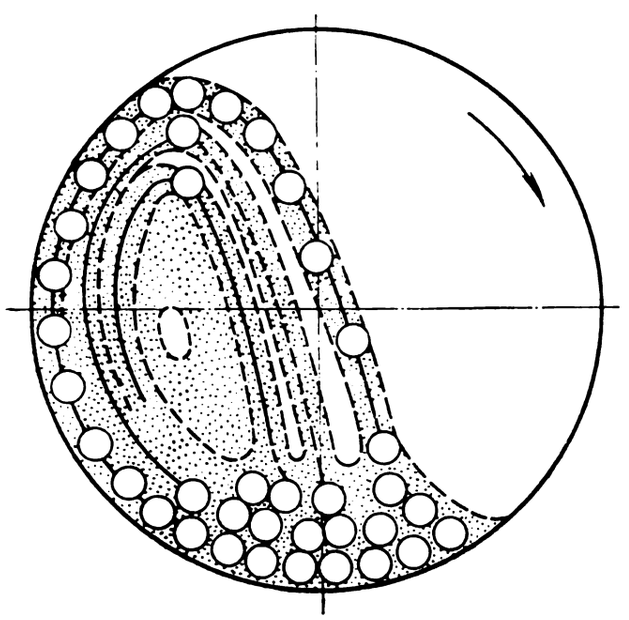

Fig. 8.10. Schematic diagram of a ball mill

Highly dispersed systems are obtained by mechanical dispersion by additionally grinding particles of coarser dispersions. To this end, a coarse dispersion is treated in a liquid medium in ball mills, paint grinders, or colloid mills where its rather large particles undergo collisions, crushing, or abrasion, depending on the type of apparatus. As a result, they disintegrate into fine particles which, owing to the stabilizer that is introduced into the dispersion medium, form a higher dispersed stable system.

The principle according to which ball mills operate can be seen from Fig. 8.10. The ball mill is a rotating hollow metallic cylinder which is partially filled up with heavy metallic or porcelain balls. It is loaded with a coarse dispersion of the substance being ground and the dispersion medium containing a stabilizer; then the cylinder is brought into slow rotary motion. Under the action of the centrifugal force, the balls are pressed to the wall and rise together with it to a certain height; then, tearing away, they fall on balls which are below and crush the particles of the dispersed phase that get between them. Of course, the particles of the balls are also abraded when the balls roll over in a ball mill.

For good dispersion, the volume of balls loaded into the mill should constitute 30-40 per cent of its total volume. When there is a large number of balls, they fall from a smaller height and, consequently, grinding is worse. When their number is small, they slide along the wall, and this also worsens grinding; in addition, the balls wear away more rapidly. The dispersion volume in a ball mill should not be more than 20 per cent of the volume of the mill.

If a substance is ground in a ball mill without a dispersion medium, particles smaller than 60 μm usually cannot be obtained. Wet grind-

ing in the presence of a stabilizer yields dispersions whose particle dimensions are close to colloidal ones.

Ball mills have several advantages over other devices for obtaining highly dispersed systems: grinding is effected in closed space without the loss of a solvent if it is volatile; the process can be continued until the required extent of grinding is attained; and the maintenance of the machine is extremely simple. A deficiency of ball mills is the considerable abrasion of balls during operation; this contaminates the dispersion being obtained and causes comparatively low productivity of ball mills.

Coarse dispersions are disintegrated in such devices as paint grinders where their particles are ground between two rotating rollers or between a rotating roller and a stationary surface. In addition, dispersion occurs here also as a result of great shearing stresses which originate in the thin layer of a liquid between rollers. By their operation, mixing rollers used in rubber production are similar to paint grinders.

The greatest dispersity can be attained by using colloid mills for dispersing a solid in a liquid. The first colloid mill designed by H. Plauson consisted of a metal sheath which was cooled with water and in which an eccentric shaft rotated at a frequency of 10,000-20,000 rpm. Metal pegs, or beaters, were fixed in several rows to the shaft. The inner wall of the metal sheath had metallic teeth between which beaters passed as the shaft rotated. A suspension of a preliminarily coarsely ground substance was fed into the sheath from the top. As the shaft rotated, the liquid was thrown off from it at a high velocity, but new portions of the liquid were simultaneously drawn in. Coarse particles were crushed in the mill owing to their collision against beaters and teeth and to abrasion. The liquid which contained dispersed particles whose dimensions were close to colloidal ones was taken out of the sheath from the bottom.

Another type of a colloid mill now widely used is represented in Fig. 8.11. It consists of a rotor (conical disc *1* resting on shaft *2*) and of stator *3*. The rotor is set in motion by means of a vertically situated motor which performs about 9,000 rpm. Working surfaces *4* of the rotor and stator are ground down to one another, and the gap between them is about 0.05 mm. A coarse suspension is fed to the mill through inlet pipe *5* under the rotating disc by a centrifugal force which develops as a result of the rotations of the rotor. Then the suspension is pressed through the gap and is removed from the mill through outlet pipe *6*. Particles suspended in a liquid experience considerable shearing stresses and are ground when the liquid passes as a thin film through the gap. The dispersity of the system obtained depends on the thickness of the gap and the speed of rotation of the rotor: the smaller the gap and the higher the speed, the greater is shearing stress and, consequently, dispersity.

Several designs of colloid mills have been elaborated. However, systems of such high dispersity as those produced by condensation are never obtained by colloid mills of even the most advanced designs.

Dispersion by ultrasound of over 20,000 vibrations per second which are not audible to the human ear is effective only when the substance being dispersed is of low strength. Such substances are

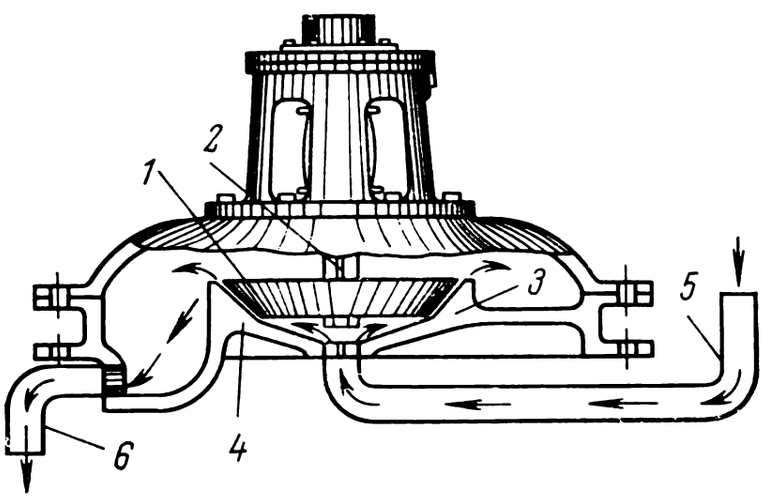

Fig. 8.11. Scheme of a colloid mill:
1—conical rotor disc; *2*—rotor shaft; *3*—stator; *4*—ground-down working surfaces; *5*—inlet pipe; *6*—outlet pipe

resins, sulphur, graphite, and gypsum. Dispersions of light metals and their alloys in organic liquids can also be obtained by ultrasound. Moreover, ultrasound can be successfully used when freshly prepared precipitates are being peptized.

Ultrasonic vibrations are usually obtained by piezoelectric oscillators which convert electric vibrations of high frequency into mechanical ones. Ultrasonic waves having a frequency of one million vibrations per second are now obtained by quartz oscillators. Ultrasonic waves of a lower frequency (about 50,000 vibrations per second) are obtained by magnetostriction oscillators whose working part is a ferromagnetic rod.

Dispersion by piezoelectric oscillators is performed in the following way. The potential difference is applied to a piezoelectric plate which is placed in a liquid having a small dielectric constant, such as transformer oil. Ultrasonic vibrations are transmitted through this liquid to a vessel containing a system undergoing dispersion.

The mechanism of dispersion of solids by ultrasound has not been studied well enough. Ultrasonic vibrations cause local, rapidly alternating contractions and expansions of a substance in a system; this results in the formation of minute recesses, or cavities, which disappear immediately under the action of external pressure. These contractions, expansions, and cavities destroy a solid, i.e., they

disperse it. Ultrasonic waves under definite conditions may cause not only dispersion, but also coagulation which occurs owing to the accumulation of particles in vibration nodes and to the movement of smaller particles towards larger ones. As a result of such coagulation, equilibrium is rapidly attained in the course of dispersion when the same amount of a substance is dispersed as that which precipitates from a sol.

Vibration grinders are now widely used for dispersion. These devices operate by frequently alternating power impulses acting on a material as a result of which a large number of weak impacts is communicated to it. This principle is the basis of operation of the vibrating mill which is a combination of a ball mill and a vibrator. The vibrator causes the body of the mill to vibrate at a frequency equal to the number of revolutions of the electric motor which sets the vibrator in motion. This causes the displacement and collision of balls, and the particles of a material are thus crushed and ground. The effectiveness of vibration mills (i.e., the intensity of the grinding forces and the capacity of the device) is determined by the frequency and amplitude of vibrations.

There are also vibration grinders without grinding bodies. In these grinders which greatly differ in design particles of the material being ground collide in intersecting flows of gas or vapour that move at a high velocity. When the velocities of motion are higher than 100 m/sec, vibration conditions of disintegration set in; therefore, not only brittle, but also plastic materials are dispersed effectively in such grinders. Such devices are advantageous because they produce a very uniform grind and there are no products of abrasion of the grinding surfaces in the ground material. In addition, such grinding devices are far more economical than ordinary mills.

Mechanical dispersion of particles of the dispersed phase is as a rule conducted in an aqueous medium. Aqueous systems can be easily converted into suspensions having a non-aqueous medium, provided the particles of these systems are wetted by organic liquids. For example, pigments are usually ground in water, then the moist pigment is mixed with oil, and hydrophobic particles of a pigment pass into oil. This technique of substituting a medium is unsuitable for highly dispersed colloidal systems obtained by condensation because particles of colloidal dimensions as a rule collect at the liquid-liquid interface when a hydrosol is being mixed together with an organic liquid.

The electrosputtering of metal electrodes, which are immersed in a dispersion medium, in a voltaic arc can be related to the dispersion methods of producing sols because the dispersed phase is formed here by the direct dispersion of a metal; solid particles of colloidal dimensions tear away from metal electrodes, enter the medium, and form a lyosol. But, on the other hand, this method

can be regarded, even if partially, as a condensation one because, at a high temperature of the arc, the metal of the electrodes becomes vapour which, coming into contact with the surrounding medium, cools, condenses, and forms colloidal particles.

The electrosputtering method was proposed by G. Bredig in 1898. He connected an ammeter, a rheostat and two electrodes made of a metal to be dispersed to a circuit of direct current of 5-10 A and 30-110 V. He put the electrodes into a vessel that contained water

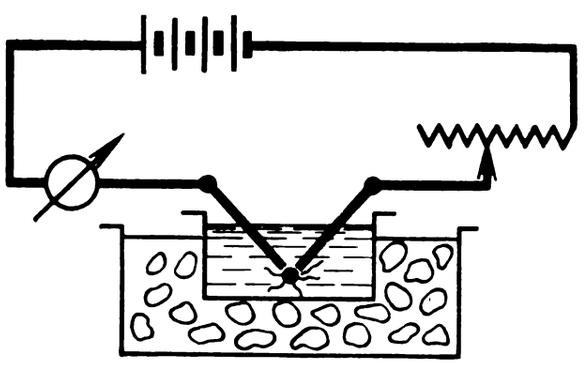

Fig. 8.12. Obtaining sols by electrosputtering according to Bredig's method

and was cooled by ice from outside. The apparatus used by Bredig is schematically illustrated in Fig. 8.12. As current passes through the electrodes, a voltaic arc originates between them under water, and a cloud of highly dispersed metal is formed near the electrodes. To obtain sols of greater stability, it is expedient to introduce traces of stabilizing electrolytes, such as hydroxides of alkali metals, into water in which the electrodes are immersed. Not only the cathode, but also the anode undergoes dispersion under the conditions described. This confirms the fact that thermal processes and vaporization phenomena are important in electrosputtering.

Owing to high temperatures created near the voltaic arc, Bredig's method can be used only for obtaining hydrosols. T. Svedberg improved this method, making it suitable for obtaining organosols. To this end, he used alternating current of high frequency instead of direct current, and he effected the electrosputerring process by immersing electrodes in a metal powder lying on the bottom of a vessel containing a dispersion medium. Electrosputtering occurs in this case as a spark gets through grains of the powder. When such a technique is used, there is far less thermal decomposition of the surrounding medium, and sols of metals in various organic liquids may be obtained.

M. Lunina and her coworkers improved the method of obtaining organosols of metals. They passed an alternating electric current through a layer of metal powder on the bottom of a vessel containing a liquid organic medium; the current caused an electric discharge at points of partial contact. Electrosputtering is used to obtain organosols of iron, nickel, aluminium, chromium, tungsten and

other metals. To increase the stability of these sols, stabilizers (usually naphthenate or stearate of aluminium) are added to a system.

Organosols of metals are widely used in the hydrogenation and reduction of various organic compounds; they are used as catalysts of combustion of liquid fuel in rockets, as fillers of plastics, glues, anticorrosive lacquers and paints, are employed in medicine for preparing medicinals, and so forth.

Obtainment of lyosols by peptization. There are the following types of peptization: peptization by washing the precipitate; peptization of the precipitate by an electrolyte; peptization by a surfactant; and chemical peptization.

Peptization by washing the precipitate consists in the removal from it of an electrolyte causing coagulation. As a result, the remaining electric double layer thickens, repulsive forces begin to predominate over attractive forces, and micelles which separated from one another are uniformly distributed in the dispersion medium owing to Brownian motion, i.e., they form a colloidal solution. This type of peptization does not require the introduction of a peptizer into a system because a stabilizer is present in the precipitate, and washing merely makes it more active.

The peptization of a precipitate by washing is often encountered in analytical chemistry where it is usually treated as an undesirable phenomenon. When the precipitate is washed with water, it often passes through a filter, and this indicates an increase in its dispersity and the formation of a hydrosol.

Let us consider, as an example, the behaviour of the Mo_2O_5 precipitate when it is washed several times with constant volumes of water at 18-20 °C; the precipitate was obtained by coagulation by various electrolytes.

As we may see, the greater the valency and radius of the coagulating ion, the more difficult is the peptization of the precipitate by washing because these ions, if they are polyvalent or have a large

Electrolyte used in coagulation	Extent of peptization
NaCl	Complete peptization after one washing
NH_4Cl	Ditto
KCl	Ditto, after two washings
Morphine chloride	Ditto, after three washings
$Sr(NO_3)_2$	Ditto, after six washings
$BaCl_2$	Traces of peptization after seven washings
$Al_2(SO_4)_3$	Ditto

radius, are retained more firmly by the precipitate and thus hinder peptization.

Peptization by electrolytes is observed when an electrolyte, one of whose ions can complete the construction of the crystal lattice of the dispersed phase or, at least, be adsorbed on its surface, is introduced into the precipitate formed in the course of coagulation. Of course, such peptization always occurs more rapidly when the precipitate is preliminarily washed with a pure solvent.

An example of peptization by an electrolyte is the addition of an iron chloride solution to a precipitate of ferric hydroxide that has been freshly prepared and washed with water. As a result of partial hydrolysis, iron oxychloride which, as we have seen, is capable of stabilizing the particles of ferric hydroxide, is formed from iron chloride. In this case, indirect peptization occurs as the substance introduced reacts at first with water, and then the product of this reaction peptizes the precipitate. The peptization of the precipitate by an electrolyte is affected not only by the ion which confers its charge on a particle, but also by an oppositely charged ion.

An example of peptization by surfactants is the peptization of a highly dispersed powder of blood charcoal by picric acid and soaps. Ferric oxide can also be peptized by soaps, and aluminium oxide, by alizarin. A highly dispersed powder of hydrophilic kaolin is peptized by humic acids. Substances of high molecular weight whose macromolecules are capable of being adsorbed on particles and of conferring on them a charge or a solvate shell often have good peptizing action. According to modern views, peptization may be caused also by the mutual repulsion of flexible molecular chains which are in thermal motion and are only partially adsorbed on the surface of colloidal particles. These views are considered at greater length in Chap. 9.

Chemical peptization occurs when a substance which is added to a system reacts with a precipitate; as a result, an electrolyte which imparts stability to the particles of the dispersed phase is formed. An example of chemical peptization is the peptization of the ferric hydroxide precipitate by hydrochloric acid which reacts with ferric hydroxide to form a stabilizer, i.e., iron oxychloride, on the surface of the precipitate particles according to the reaction

$$Fe(OH)_3 + HCl \longrightarrow FeOCl + 2H_2O$$

4. PURIFYING COLLOIDAL SYSTEMS

Lyosols often contain impurities of low molecular weight besides micelles, a stabilizing electrolyte, and a solvent. For example, the sol of silver iodide which is obtained by a reaction between silver nitrate and potassium iodide always contains a considerable amount of an indifferent electrolyte, potassium nitrate. In other cases, elec-

trolytes and other impurities of low molecular weight may get into colloidal systems when the initial products are contaminated or owing to other causes.

Since extraneous electrolytes astabilize colloidal systems, the sols obtained must often be purified. Impurities of low molecular weight can be removed from lyosols by dialysis, electrodialysis, and ultrafiltration.

Dialysis. We have already considered this simple method of purifying colloidal systems at the beginning of the textbook. A simple dialyzer consists of a little bag made of semipermeable material into which the liquid to be dialyzed is poured. The bag is then put into a vessel containing water.

There are now many advanced designs of dialyzers in which dialysis is effected more rapidly by enlarging the surface through which dialysis occurs, reducing the layer of the liquid to be dialyzed, replacing more frequently or even continuously the external liquid, and by heating which accelerates diffusion.

The nature of the semipermeable membrane may be diverse, depending on the system which is subjected to dialysis. Formerly, bull's bladder or parchment was used as a membrane. Today, membranes made of collodion, i.e., a solution of cellulose nitrate, are more commonly used. These membranes are very convenient because they can be made with pores of any diameter. The required porosity of the collodion membrane is ensured by selecting both a solvent for cellulose nitrate and the conditions for drying the film obtained. In purifying organosols which dissolve the collodion membrane made of cellulose nitrate, a film prepared of cellophane or denitrated collodion is used for dialysis.

Long dialysis removes not only impurities from a solution, but also the stabilizer, and this may astabilize and coagulate a system.

Electrodialysis. Since impurities of low molecular weight in sols are usually electrolytes, dialysis may be accelerated by applying an electric field to the liquid being dialyzed.

Many designs of electrodialyzers have been proposed. The scheme of a relatively simple electrodialyzer used by Pauli is illustrated in Fig. 8.13. It consists of three glass chambers which are separated from one another by semipermeable partitions. Electrodes are fixed in the side chambers. Distilled water, being an external liquid, is continuously fed into these chambers via tubes; water is drained off via other tubes after electrolytes diffuse into it from the central chamber. The sol to be purified is put into the central chamber provided with a stirrer to stir the sol in electrodialysis. Electrodialysis is more effective after preliminary purification by ordinary dialysis when the rate of diffusion between the sol and water is low owing to the drop in the gradient of electrolyte concentration; then, elec-

tric fields of high voltage can be applied without greatly heating the sol.

A change in the transport numbers of ions in the capillaries of a semipermeable membrane in comparison with the same numbers characteristic of a solution is important to electrodialysis. These

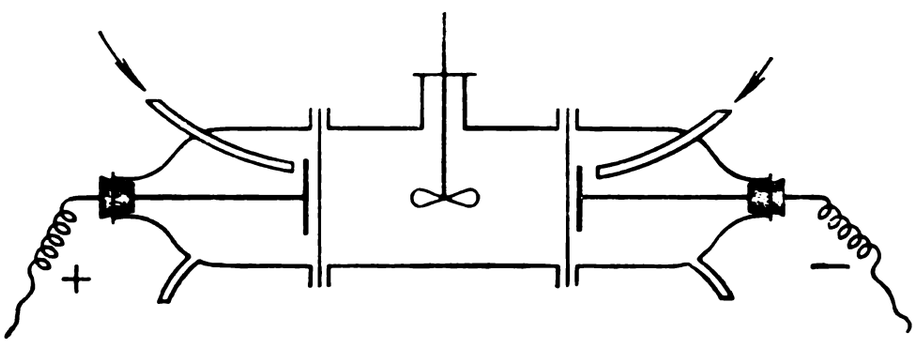

Fig. 8.13. Scheme of the construction of an electrodialyzer

changes in transport numbers were discovered by J. Hittorf as early as 1902 and then were confirmed by other authors, particularly, by I. Zhukov and his school.

Membranes made of cellulose and parchment, and also ceramic diaphragms, become negatively charged in electrolytic solutions. Other semipermeable membranes, such as those made of tanned gelatine, conversely, become positively charged in electrolytic solutions. When a diaphragm is negatively charged, the transport of electricity by anions diminishes with the pore diameter and becomes zero at the limit. Then, electricity is transferred only by cations. If the diaphragm is positively charged, an opposite phenomenon is observed. When the capillary diameter remains the same, the change in the transport numbers is the greater, the higher is the electrokinetic potential of the capillary walls.

All these phenomena can be explained if we assume that there is an electric double layer on the surface of the diaphragm capillaries. Indeed, let us imagine a capillary which has a negatively charged surface and is filled with a dilute electrolytic solution. Apparently, cations predominate in the diffuse layer of such a capillary. If the capillary diameter is large in comparison with the thickness of the electric double layer, the difference in the ratio between the concentration of cations and anions in the capillary and that in the solution outside the capillary is not great, and the transport numbers in the capillary scarcely differ from those in the solution. However, as the capillary diameter decreases and becomes commensurable with the thickness of the electric double layer, the concentration of cations grows in the capillary, and this causes an increase in cation transport numbers and a decrease in anion transport numbers. When the capillary diameter is double the thickness of the electric double layer, the change in the transport numbers will be maximum. The change in the ratio between the concentrations of cations and

anions in a capillary having a negatively charged surface when the diameter of a capillary is reduced can be seen in Fig. 8.14. The great permeability of positively charged membranes for anions can be explained in a similar way.

According to such an explanation of the change in the ion transport numbers as the diameter of membrane pores decreases, the

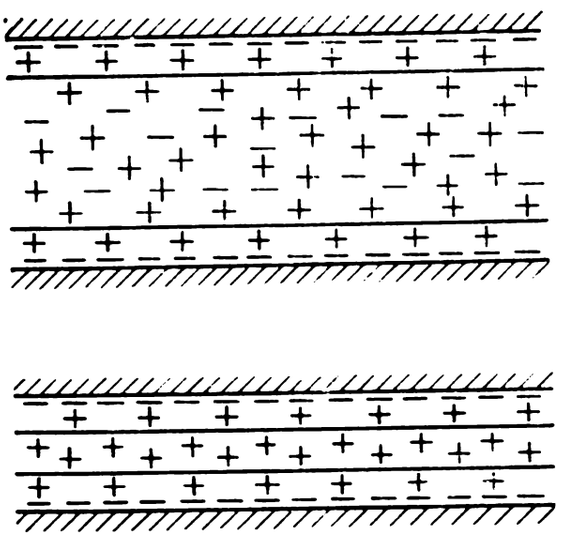

Fig. 8.14. Change in the ratio between concentrations of cations and anions in a capillary having a negatively charged surface when the diameter of a capillary decreases

numbers should apparently depend on the concentration of electrolytes in capillaries. A decrease in the concentration of an electrolyte thickens the diffused layer and should bring about a greater change in the transport numbers. An inverse relationship should be observed when the concentration of electrolytes increases. These conclusions were confirmed experimentally.

In electrodialysis, the concentrations of electrolytes in the central chamber of the electrodialyzer can change only when the electrolyte transport numbers change along the section of the electrodialyzer. As Zhukov indicates, such a change in the transport numbers can occur owing either to a change in the transport numbers in the diaphragm pores as compared with that in the free solution, or to a change in the composition of an electrolyte in the chambers. The latter phenomenon is observed in an operating electrodialyzer where acid is formed in the anode chamber, and alkali, in the cathode one. In this case, the concentration of an electrolyte in the central chamber can decrease even if electrochemically inactive diaphragms, which have pores of sufficiently large dimensions and do not change the transport numbers, were used because, as acid and alkali accumulate in the electrode chambers, the H^+ and OH^- ions forming water begin to enter the central chamber in exchange for the outgoing ions of the electrolyte.

Electrodialysis can be considerably accelerated by using electrochemically active membranes which change transport numbers. If a negatively charged membrane is put on the cathode side of a three-chamber dialyzer, it will increase the cation transport number; the positively charged membrane on the anode side will increase the anion transport number. The difference in the ion transport numbers between membranes can thus be increased considerably. Such membranes are known as ideal electrochemically active ones. The difference between transport numbers in this case will reach unity, and current efficiency will be 100 per cent.

Electrodialysis is used not only in laboratory investigations, but also in technological processes. For example, it is used to remove salts from whey. After purification, whey which contains large amounts of valuable lactose and proteins is used for making foodstuffs. Much of the lactose would have been lost if ordinary dialysis were used for purification.

Ultrafiltration. Ultrafiltration is dialysis effected under pressure. In essence, it is not a method of purifying sols, but only a method of concentrating them. In this case, an important fact is that only the concentration of the dispersed phase increases while the composition of the dispersion medium remains almost the same.

Of course, if after partial ultrafiltration the sol thus obtained is diluted with a pure solvent to the initial content of the dispersed phase, it will contain less substances of low molecular weight, but also less stabilizing electrolytes.

Ultrafiltration is sometimes used to obtain an intermicellar liquid. But electrolytes may be adsorbed on the filter during ultrafiltration, and the composition of the ultrafiltrate obtained may not be identical with that of the dispersion medium. Moreover, membrane equilibrium (or Donnan effect) is then established, being characterized by the unequal distribution of electrolytes on both sides of the membrane (see Chap. 14).

Using filters of various porosity, ultrafiltration may be employed for dividing colloidal systems into fractions of greater monodispersity and for approximately determining their dispersity. However, the pore dimensions of most membranes are in a rather wide range, and therefore it is almost impossible to obtain entirely monodispersed systems.

Many devices for ultrafiltration have been proposed. Since ultrafiltration is always performed under pressure, the membrane in all the devices for ultrafiltration either is superimposed on a plate that has small openings and serves as a support for the membrane or is directly obtained on the walls of an unglazed porcelain vessel. In particular, the Bechhold ultrafilters are obtained by depositing a dilute solution of collodion on the walls of a porous porcelain vessel and then drying it.

9

STABILITY AND COAGULATION OF COLLOIDAL SYSTEMS *

Typical colloidal systems, unlike molecular solutions, are heterogeneous, and thermodynamically and aggregatively unstable owing to an interface between particles and the dispersion medium. That is precisely why the stability of colloidal systems is the central problem in colloid chemistry whereas coagulation constitutes the most important mechanism of the transition to a more stable state for typical colloidal systems.

The stability and coagulation of colloidal systems are of great practical importance in geology, agriculture, biology, and technology. No wonder many investigations are carried out in this field.

The instability of sols may also be exhibited in the coarsening of particles due to either the disappearance of finer ones or their increase in size. The coarsening of particles in sols is similar to isothermal distillation during which large drops or crystals grow in closed volume at the expense of small ones as a result of the high pressure of saturated vapour of small drops or crystals. Such sol instability, yielding coarse particles, is exhibited the more rapidly, the higher is the solubility of the dispersed phase. The rate of the process in the liquid medium can be changed by controlling the solubility of the dispersed phase, i.e., by changing either the composition of the dispersion medium or temperature. That is what is done in analytical chemistry to enlarge minute particles which pass through a filter. However, owing to a low solubility of the dispersed phase, colloidal systems are destroyed very slowly as coarse particles grow at the expense of minute ones; the researcher working in colloid chemistry rather rarely deals with such a loss in stability.

Coagulation which causes aggregation is far more important to colloidal systems.

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* The first three sections of this chapter were written by B. Deryagin.

Colloidal systems possess different aggregative stability. Some systems exist for only several seconds after their formation, but there are many colloidal systems which exist for a long time. For example, typical hydrophobic sols of silver iodide and of arsenic sulphide are very stable and can be kept for years if extraneous electrolytes have been removed from them. The long existence of fundamentally unstable colloidal systems apparently cannot be attributed only to the low concentration of a sol and, consequently, to rare collisions between particles because the concentration of a dispersed phase can be brought up to 10 per cent and even more in purified sols.

The aggregative stability of disperse systems greatly depends on the composition of the dispersion medium and can be abruptly changed by introducing even very small amounts of extraneous electrolytes into it. Colloidal systems can be divided into two classes according to the effect of added electrolytes on stability: lyophobic and lyophilic systems. In lyophobic systems, the coagulation rate sharply increases as electrolytes are added. After passing a certain limit, i.e., critical concentration, the coagulation rate attains a maximum value which characterizes rapid coagulation. Lyophilic colloidal systems coagulate if the concentration of the electrolyte added is very high, being several moles per litre.

The critical concentrations of electrolytes in lyophobic systems (unlike lyophilic ones) sharply diminish with a growth in the charge of counterions, i.e., ions bearing a charge opposite in sign to that of colloidal particles.

Taking into account these specific features of the aggregative instability of lyophobic systems, say of metal sols, Hardy assumed that the stability of lyophobic sols is caused by the electric charge of their particles, being detected in electrophoretic phenomena. When this was confirmed, it became clear that the mechanism of stability and the nature of lyophobic dispersed systems differ from those of lyophilic ones.

Lyophobic systems have been studied most substantially and successfully, especially in the theoretical sense, and we will consider their stability and coagulation first of all.

Some authors interpreted the aggregative stability of lyophobic colloidal systems in thermodynamic terms. For example, A. March took into account the positive free energy of the interface, the diminution in free energy as an electric double layer was formed on particles, and the entropy of a system; he tried to determine the conditions under which a factor promoting coagulation is equilibrated with a counteracting factor, thus making a colloidal system aggregatively stable. However, with some exceptions (see Chap. 8), all these attempts failed because the authors did not take into account that the interface between a particle and the dispersion medium hard-

ly changed when particles sticked together (see Chap. 1); thus the change in energy must be calculated with regard to the action of the attraction forces between particles. These forces, together with repulsive forces, determine the aggregative stability of a system.

In this connection, the aggregative stability of a system usually implies that the coagulation process is slow, i.e., its nature is kinetic and not thermodynamic. Even when the processes of aggregation and disaggregation equilibrate each other, the entire system may not be in thermodynamic equilibrium.

1. KINETICS OF COAGULATION

Before discussing the causes of the stability and coagulation of lyosols, let us consider the kinetics of coagulation, the theory of which was elaborated much earlier than that for the stability of colloidal systems.

Coagulation can be either rapid or slow. Rapid coagulation occurs when all particles in Brownian motion stick together as they approach each other. In slow coagulation, only some particles stick together upon approach because the electric double layer or the solvate shell partially remains on the surface of a colloidal particle. Therefore, both terms are used quite nominally.

The theory of the kinetics of rapid coagulation was worked out by Smoluchowski on the basis of the following principles. The forces of attraction and repulsion act between sol particles; the repulsive forces weaken when an electrolyte is added and disappear when its concentration is high enough to cause rapid coagulation. A further addition of the electrolyte does not accelerate coagulation. The particles of such an astabilized sol, as they approach one another closely enough in the course of Brownian motion, stick together under the action of forces of molecular attraction to form an aggregate which then undergoes Brownian motion as a single entity. Smoluchowski did not study the nature of the forces acting between particles.

To study the kinetics of coagulation, it was necessary to determine the change in the concentration of sol particles during coagulation. This can be done by counting the particles with the aid of an ultramicroscope. But it takes a very long time to determine the numerical concentration in this way whereas coagulation usually occurs very rapidly; therefore, by the time counting is finished, the concentration of particles in a sol will differ from their initial concentration. This difficulty was overcome by adding to a sol, at a certain moment, a stabilizer ceasing coagulation induced by an electrolyte which had been already introduced. In such a stabilized sol, the numerical concentration of particles no longer changes and it can be determined with an ultramicroscope. Gelatin was often used as a stabi-

lizer for ceasing coagulation. At present, the method of counting particles in a stationary volume is no more used.

The coagulation process is now studied by counting flowing particles. The flow ultramicroscope was designed by Deryagin and Vlasenko (see Chap. 2). It can be used to determine the numerical concentration much more rapidly than the old method allowed without interrupting coagulation. At the same time, the new technique eliminates many sources of errors inherent in the old method of measuring the numerical concentration of a sol. This method has been recently improved by A. Smith.

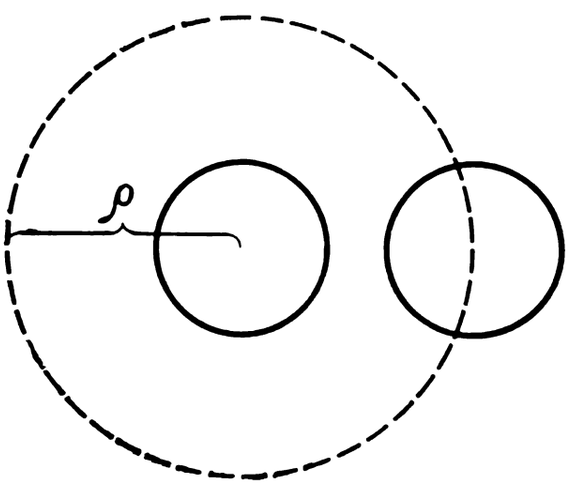

Fig. 9.1. Diagram explaining the sphere of action of particles in rapid coagulation

When Smoluchowski was working out his theory, he assumed that the rate of rapid coagulation, i.e., a change in the numerical concentration of particles per unit time, depended on ν, the numerical concentration of a sol, on the velocity of Brownian motion, characterized by D, the coefficient of the Brownian diffusion of particles, and on the critical distance ρ by which the centres of two particles should approach one another to stick together. Distance ρ can be greater than the diameter of colloidal particles (Fig. 9.1). Thus, for a sphere of radius ρ whose centre coincides with that of a particle, the other particle will adhere to it only when the centre of the second particle touches the surface of the sphere, known as the absorption sphere. When distances were larger than ρ, Smoluchowski completely neglected the action of the molecular forces of attraction on the Brownian motion of particles and on their approach.

According to Smoluchowski, in rapid coagulation, single particles collide with one another to form double particles which, colliding with single particles, form triple ones, and so forth. Collisions between complex particles are also possible. Three or more single or complex particles can collide simultaneously, but, to simplify his theory, Smoluchowski did not take such collisions into account because of their very low probability.

Denoting the numerical concentrations of particles consisting of one, two, three, and more primary particles by ν_1, ν_2, ν_3, . . ., we can write that at the beginning, when time $\tau = 0$,

$$\nu_1 = \nu_0 \text{ and } \nu_2 = \nu_3 = \ldots \nu_n = 0$$

After time τ,

$$\nu = \nu_\tau = \nu_1 + \nu_2 + \nu_3 + \ldots$$

where ν is the final numerical concentration.

In this case, the following inequality will apparently be observed:

$$\nu < \nu_0$$

Smoluchowski believed that the coagulation process can be formally regarded as a second-order reaction. The coagulation rate should then be directly proportional to the square of the numerical concentration which determines the probability (or frequency) of the approach of particles to distance ρ:

$$-d\nu/d\tau = k\nu^2 \tag{9.1}$$

where k is a constant which characterizes the probability of approach.

The derivative $d\nu/d\tau$ has a negative sign because the numerical concentration ν drops in the course of time τ.

According to Smoluchowski, the constant k, which depends on the coefficient of Brownian diffusion D and distance ρ, is expressed as

$$k = 4\pi D\rho \tag{9.2}$$

Eq. (9.2) can be derived in the following way. Let the coordinate origin coincide with the centre of a randomly selected particle. In this system, the coordinates of displacement of other particles Δ' will actually be equal to the displacements with respect to the randomly selected particle, i.e.,

$$\Delta' = \Delta_i - \Delta_1$$

where Δ_i = actual displacement of an ith particle;

Δ_1 = displacement of the particle at the coordinate origin.

Apparently, in squaring both members of the equation and averaging out for time τ, we obtain

$$(\overline{\Delta'})^2 = (\overline{\Delta_i - \Delta_1})^2 = \overline{\Delta_i^2} - 2\overline{\Delta_i\Delta_1} + \overline{\Delta_1^2} \tag{9.3}$$

In this equation, the line above the symbol of the quantity implies that the mean value of the quantity is taken.

In Brownian motion, the displacements of both particles are independent of one another. Therefore, as can be strictly proven statistically, the order of the operations of averaging and multiplying can be reversed:

$$\overline{\Delta_i\Delta_1} = \overline{\Delta_i} \cdot \overline{\Delta_1}$$

But $\overline{\Delta}_i = 0$ and $\overline{\Delta}_1 = 0$ because all the directions of displacements are equally probable. Therefore, $\overline{\Delta_i\Delta_1} = 0$ and

$$(\overline{\Delta'})^2 = \overline{\Delta_i^2} + \overline{\Delta_1^2} = 2\overline{\Delta_i^2} \tag{9.4}$$

Thus, the mean squares of the displacements of all the particles relative to the first one are doubled. Owing to the relationship between $\overline{\Delta_i^2}$ and diffusivity, we can say that the Brownian motion of

the other particles relative to the first one is characterized by double diffusivity D'. As a result, particles will occasionally approach the first one to the critical distance ρ between their centres.

Let us calculate the number of such approaches without taking account of the complications caused by changes in Brownian motion as a result of the sticking together of particles. Let us suppose that the particle is absorbed, as it were, by the central one after particles approach one another to the distance ρ between their centres. Suppose that the particles are in a very large volume, and that numerical concentration ν is equal to ν_τ at a given moment of coagulation. But the particle concentration approximates zero in the immediate proximity of the surface of the absorbing sphere because the probability of a particle near the absorbing sphere to get into it is very great and the probability of avoiding this is very small, owing to chaotic Brownian motion. The values of ν_τ are rapidly attained when moving away from the sphere of radius ρ. The displacement of particles' ensemble, which randomly wander independently of one another, is described by the diffusion equation. Suppose that the particle concentration $\nu(R)$ depends only on distance R from the coordinate origin to which the diffusion flow, caused by the absorption of particles by the sphere of radius ρ, is directed. In this case, it follows from the diffusion laws that

$$Q = D's\frac{d\nu(R)}{dR} = D'4\pi R^2\frac{d\nu(R)}{dR} \tag{9.5}$$

where Q is the number of particles which pass through the surface s of sphere having radius R towards the central particle per unit time.

Q is apparently equal to the number of particles absorbed by the central particle when they approach it per unit time, i.e., Q is equal to the sought frequency of the acts of aggregation involving the central particle.

Taking account of the boundary condition

$$\nu(\rho) = 0 \tag{9.6}$$

which follows from the fact that particles are absorbed by the central particle after reaching sphere ρ, and integrating Eq. (9.5), we obtain

$$\nu(R) = \frac{Q}{4\pi D'}\left(\frac{1}{\rho} - \frac{1}{R}\right) \tag{9.7}$$

Taking account of another boundary condition

$$\nu(\infty) = \nu_0 \tag{9.8}$$

we obtain

$$Q = 4\pi D'\nu_0\rho \tag{9.9}$$

The total number of approaches of all particles per unit volume can be determined by multiplying Q by the numerical concentration ν and dividing the product by 2 because otherwise every pair of particles will be counted twice. Substituting D' by $2D$, we obtain

$$-d\nu/d\tau = 4\pi D\rho\nu^2 \tag{9.10}$$

Comparing this equation with Eq. (9.1), we find the value of constant k in Smoluchowski's equation (9.2):

$$k = 4\pi D\rho$$

Smoluchowski's equation presupposes the initial moment of coagulation before which particles do not stick together. Therefore, at the initial moment, the central particle is surrounded with particles whose concentration is equal to ν_0 everywhere. As a result, at the beginning of the coagulation process, the frequency of approaches and agglomeration is greater than quantity Q in Eq. (9.9). However, owing to the high initial frequency of approaches, the concentration of particles near the central one diminishes very soon to zero, and the distribution of particles will obey Eq. (9.6) in fractions of a second. The coagulation rate will then obey Smoluchowski's equation.

But there will be deviations from Smoluchowski's law after a certain lapse of time, mainly because the coefficient k in Eq. (9.2) for the approach of two particles assumes a different value when an aggregate of agglomerated particles approaches another aggregate or a particle.

After writing Eq. (9.1) as

$$-d\nu/\nu^2 = k\,d\tau \tag{9.11}$$

and integrating it from ν_0 to ν and from 0 to τ, we obtain

$$1/\nu - 1/\nu_0 = k\tau$$

whence the numerical concentration of a sol at moment τ will be

$$\nu = \frac{\nu_0}{1 + k\nu_0\tau} \tag{9.12}$$

Introducing the time of coagulation θ, in which the number of particles is halved, we can write

$$k\nu_0 = 1/\theta \tag{9.13}$$

The main equation (9.12) can then be represented as

$$\nu = \frac{\nu_0}{1 + \tau/\theta} \tag{9.14}$$

Knowing ν_0 and ν for various values of τ, we can calculate θ and k by Eqs. (9.14) and (9.13).

The relative changes in the total number of particles $\Sigma\nu$ and the number of particles ν_1, ν_2, ν_3 . . . per unit volume of a sol as a function of τ/θ are graphically illustrated in Fig. 9.2. It follows from Eq. (9.14) that $1/\nu$ is the linear function of time τ. This corollary of the theory has often been confirmed experimentally.

Smoluchowski's theory makes it also possible to calculate distances ρ by which the centres of two particles should approach one another to stick together.

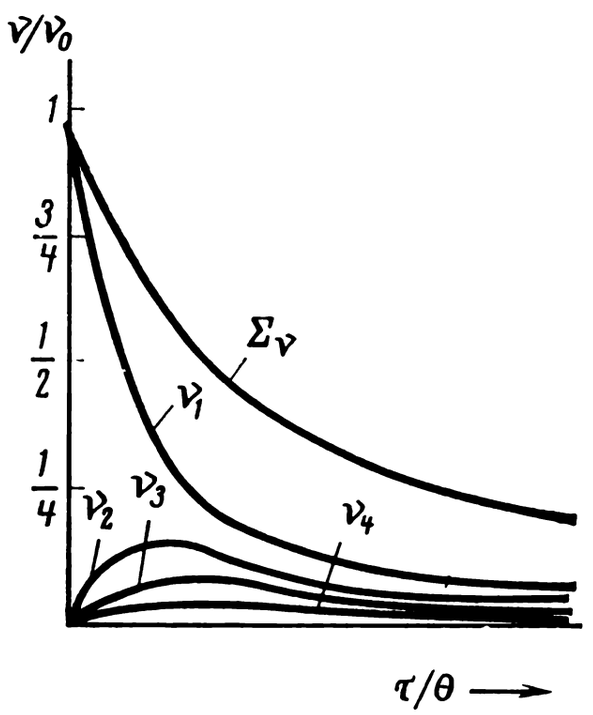

Fig. 9.2. Relative number of particles of a different order as a function of τ/θ in rapid coagulation

From Eq. (9.13),

$$\theta = \frac{1}{k\nu_0} = \frac{1}{4\pi D\rho\nu_0}$$

and, according to Einstein,

$$D = kT\frac{1}{6\pi\eta r} \qquad (9.15)$$

where k = Boltzmann constant;
η = dynamic viscosity of the dispersion medium;
r = particle radius.

Then, combining the last two equations, we obtain

$$\theta = \frac{6\eta r}{4\rho\nu_0 kT}$$

or

$$\frac{\rho}{r} = \frac{3\eta}{2\nu_0 kT\theta} \qquad (9.16)$$

Experimentally, $\rho/r = 2.3$; thus, distance ρ is rather close to $2r$, i.e., attractive forces begin to operate only when particles approach one another to very short distances at which the energy of molecular attraction becomes much greater than that of thermal motion and, consequently, Brownian motion ($3/2kT$).

Smoluchowski's concepts explain the coagulation of monodispersed sols. H. Müller elaborated a similar theory to explain the coagulation of polydispersed systems. He showed that particles of various dimensions always aggregate more rapidly than the same ones. In addition, coarse particles act like coagulation "nuclei"; aggregates formed at the initial stage of the coagulation of an almost monodispersed gold sol can act likewise, as Deryagin and Kudryavtseva have shown. Müller's principles are quite correct only when sol particles are considerably large. Müller's theory explains the autocatalytic nature of coagulation whose rate may gradually grow in the course of time. He also showed that coagulation accelerates if particles are elongated because rotary motion, which makes the

collision of such particles more probable, is superimposed on translatory Brownian motion.

As we have often emphasized, Smoluchowski's theory is applicable only to rapid coagulation. He assumed that his theory could be extended to slow coagulation when particles are not completely astabilized. In this case, ε, effectiveness of particle encounters, should be introduced into Eq. (9.12) which describes the coagulation process:

$$v_\tau = \frac{v_0}{1 + \varepsilon k v_0 \tau} \tag{9.17}$$

However, a somewhat different meaning should be imparted to the parameter ε, as follows from the coagulation theory of N. Fuchs applicable to particles whose forces of interaction change with distance according to any law.

According to Smoluchowski, there are no forces of interaction between particles until they approach one another to a distance ρ. To take account of the long-range forces of particles as a function of the distance between their centres, Fuchs supplemented Eq. (9.5) with a term expressing the drift of particles towards the central particle under the action of attractive forces F:

$$Q = 4\pi R^2 (D' \, dv/dR + 2\beta F v) \tag{9.18}$$

where β is the mobility of particles in a viscous medium, which is equal to the ratio of its velocity to the acting force; figure 2 in front of β is introduced because both particles actually move towards one another.

According to Einstein, $\beta = D/kT$; consequently, $2\beta = D'/kT$. Then, substituting force F by dU/dR (where U is the potential energy of molecular interaction between two particles) and integrating Eq. (9.18), we will obtain the following instead of Eq. (9.9):

$$Q = \frac{4\pi D' v_0}{\int_\rho^\infty e^{U(R)/kT} \cdot dR/R^2} \tag{9.19}$$

At $U(R) = 0$, Eq. (9.9) is obtained again. Eq. (9.19) was originally derived by Fuchs for aerosols in order to take account of coagulation acceleration caused by the attraction of oppositely charged particles. Here, the potential energy of interaction is negative, and the coagulation rate grows.

In general, we can obtain from Eq. (9.19), instead of Eq. (9.10),

$$-\frac{dv}{d\tau} = \frac{4\pi D \rho v^2}{\int_\rho^\infty e^{U(R)/kT} \cdot dR/R^2} \tag{9.20}$$

and, instead of Smoluchowski's constant k, we can obtain a quantity which is smaller by W times, where

$$W = \rho \int_{\rho}^{\infty} e^{U(R)/kT} \cdot dR/R^2$$

The quantity W is known as the retardation factor. The equation for slow coagulation is obtained by substituting $1/W$ for ε. Thus, Fuchs' theory gives an interpretation of Smoluchowski's coefficient ε.

In some cases, repulsive forces predominate between particles. Then, $U(R) > 0$, and the value of Q becomes extremely small if $U(R)$ is much greater than kT for some values of R. This means that the coagulation rate will diminish so greatly that we could speak of the practical aggregative stability of a system.

Deryagin and Kudryavtseva studied the kinetics of coagulation with a flow ultramicroscope (similar to the flow ultramicroscope for aerosols designed by Deryagin and Vlasenko). The flow ultramicroscope can be used to determine, in 2-3 minutes, the numerical concentration of hydrosols up to 10^{10}-10^{11} particles per cubic centimetre; other techniques of counting particles are suitable for measuring the concentration only up to 10^4-10^5 particles per cubic centimetre. When sols are sufficiently concentrated, the flow microscope can be employed to observe not only rapid coagulation, but also slow coagulation which corresponds to low values of ε, without taking too much time.

Fig. 9.3 shows the graphs of $1/\nu$ as a function of time τ which has passed since the beginning of the coagulation process for a rather low dispersed blue hydrosol of gold; the family of curves corresponds to various concentrations of a coagulating electrolyte. At a high concentration of an electrolyte (curves *3* and *4*), when the potential barrier* disappears, the kinetics of coagulation is characterized by linear dependence, which follows from Smoluchowski's theory. According to V. Muller, the slope of the straight line to the abscissa is somewhat smaller because, at close distances, the viscous resistance of a liquid interlayer to the approach of spherical particles is larger than the resistance calculated by the Stokes formula. The dependence (curves *1* and *2*) is not linear at low electrolyte concentrations. Curve *2* is typical in this respect. The initial rise of the curve is followed by a segment which is almost parallel to the abscissa; then, the curve rises again in the course of time. According to Deryagin and Kudryavtseva, the initial rise of the curve and, con-

* Students should be familiar with the concepts of potential, or energy, barrier and potential hole from the textbook of physical chemistry. These concepts in their application to colloidal systems are dealt with at greater length in the following sections of this chapter.

sequently, a diminution in the numerical concentration of a sol imply the formation of aggregates from binary particles. At low concentrations of an electrolyte, the potential hole has comparatively little depth, energy interactions are not great, and therefore binary particles disintegrate at a sufficient frequency.

When a definite concentration of binary particles is attained, their disintegration is counterbalanced by the sticking together

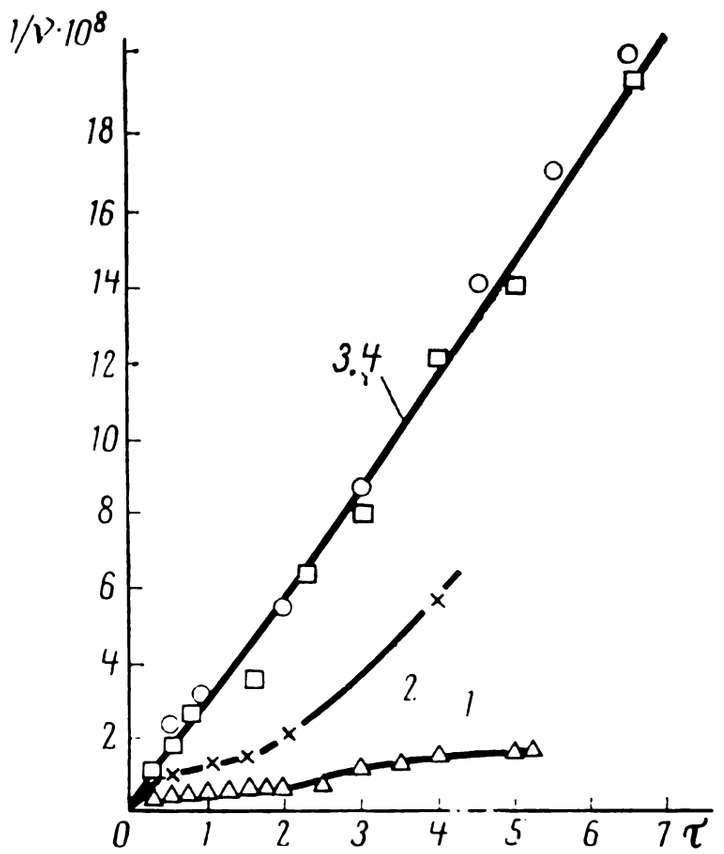

Fig. 9.3. Kinetics of coagulation of a blue hydrosol of gold in the presence of potassium chloride.
Concentration of a coagulating electrolyte (in mol/l):
1—5×10^{-3}; *2*—1×10^{-2}; *3*—5×10^{-2}; *4*—1×10^{-1}

of particles, as a result of which the numerical concentration of a sol becomes constant. At a certain moment, a third particle adheres to one of the binary particles to form an aggregate of three particles. The binding energy of each of these three particles doubles that of the particle which is in a binary aggregate, making the former quite stable. At the same time, aggregates grow further as new particles are bound. Indeed, at a certain moment, as can be seen by "flashes" in the field of vision of a flow ultramicroscope brighter particles appear among dim ones, and coagulation accelerates. This explains why the curves have an inflection. At higher concentrations of an electrolyte, the energy barrier decreases and the potential hole deepens; as a result the horizontal segments of the graph shorten and finally disappear, but the curves remain S-shaped. Thus, in studying coagulation, account should be taken of not only aggregation, but also of disaggregation.

G. Martynov and V. Muller have evolved these principles further. Under definite conditions, aggregate equilibrium may be established between single particles and aggregated ones. The probability of disintegration of large aggregates is less than that of binary ones; however, a decrease in the number of single particles at the final stage of coagulation can reduce the rate of formation of new aggregates so greatly that coagulation will be counterbalanced by the rate of disaggregation. Thus, equilibrium can be established between a coagulate and the remaining dilute sol. But this phenomenon is not general because there are sols which coagulate irreversibly; the behaviour of gold sols discovered by Kudryavtseva is apparently determined by the fact that the surface of gold particles becomes partially hydrophilic as they adsorb organic components which remain in a sol after its preparation.

As C. Goodeve et al. have shown, the rheological behaviour of thixotropic suspensions (see Chap. 10) can be understood by taking account of aggregation and disaggregation and their acceleration in the gradient flow.

Disaggregation in coagulation should be distinguished from peptization, i.e., disaggregation as a result of a change in the ionic composition of the dispersion medium which we have dealt with in Chap. 8. In this case, peptization is caused by the intensification of the electric constituent of disjoining pressure and by the diminution in the depth of a potential hole.

2. STABILITY OF THIN LIQUID LAYERS AND THE ENERGY OF INTERACTION BETWEEN THE SURFACES OF TWO BODIES

The forces of interaction between colloidal particles, exhibited when the liquid interlayers separating them grow thinner, can either accelerate coagulation or retard it. To understand the role of such interlayers and the mechanism of their stabilizing action, let us consider their behaviour exemplified by a simple scheme when a liquid interlayer separates the parallel surfaces of two plates. In this case, the separating interlayer has the same thickness everywhere and its edges border on the dispersion medium into which both plates are immersed.

When the interlayer is sufficiently thin (less than 1 μm), the hydrostatic pressure in it differs from the pressure in the surrounding liquid by the value of disjoining pressure which is a function of the interlayer thickness. Therefore, in order to maintain the equilibrium at which the interlayer thickness remains constant, a force that counterbalances the disjoining pressure of the interlayer must be applied to the plates. Disjoining pressure Π can be found by determining the

value of counterbalancing pressure. Disjoining pressure is negative if hydrostatic pressure in the interlayer is lower than the bulk pressure or the plates are attracted to one another.

Let us consider the nature of the forces which determine disjoining pressure and its dependence on the thickness of the gap between the plates.

Molecular forces of attraction. It is necessary above all to consider the forces of molecular attraction that act between the surfaces of any bodies of the same or different nature.

The law of molecular attraction is exhibited most simply in the interaction of two molecules in the absence of other molecules which can change the force of molecular attraction. F. London was the first to show with the aid of quantum mechanics that the attractive force F_m changes in inverse proportion to the seventh power of the distance r between molecules whereas U_m, the molecular energy of attraction, is inversely proportional to the sixth power of the distance:

$$U_m = -a/r^6 \tag{9.21}$$

$$F_m = -dU_m/dr = -6a/r^7 \tag{9.22}$$

The negative sign in Eq. (9.21) indicates the loss in energy as molecules approach each other, and the negative sign in Eq. (9.22) shows that the attractive force increases as the distance r decreases. The constant a changes within a rather wide range, depending on the nature of both molecules. To determine the effect of potential energy on particle motion, the quantity U_m should be divided by kT, the energy of the thermal motion of molecules:

$$\frac{U_m}{kT} = -\frac{b}{r^6}$$

where b is equal to a/kT.

The ratio U_m/kT becomes very small at distances of several molecular radii.

Eqs. (9.21) and (9.22) are applicable also when there are many molecules, but the mean distances between them are great in comparison with their radii, as is the case, for example, in gases. Then, the total energy of all the molecules can be found by summing up Eq. (9.21) for all the pairs of molecules. The value of constant a can be found when the correction in the van der Waals equation, which takes account of the mutual attraction of molecules, is known.

Such a summation of molecular interactions can be used as a first approximation to calculate the resultant force with which two plates, separated by a flat gap having a width h, are attracted to one another. To this end, according to Sheludko, let us first determine the energy of interaction U'_m of a molecule with all the molecules

of a plate located at a distance of r_0 from it (Fig. 9.4). The plate is assumed to be much thicker than h, and also than the radius of

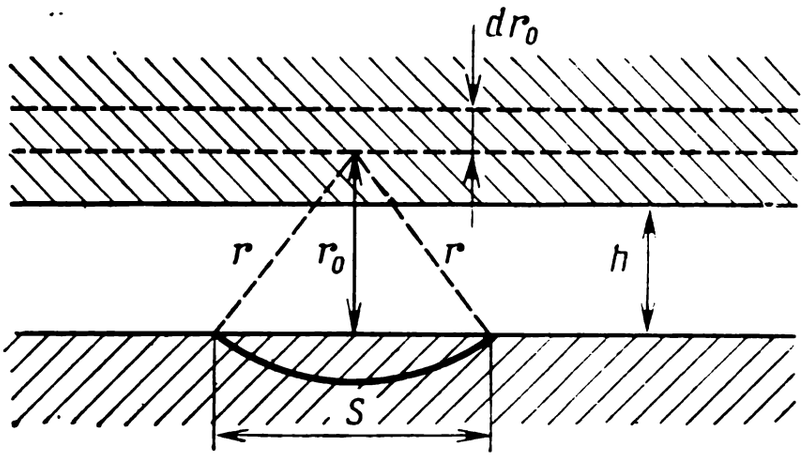

Fig. 9.4. Illustrating the calculation of the energy of attraction to a thick plate

molecular action. In this case, summation for all the molecule pairs can be replaced, without a noticeable error, by integration in the range between r_0 and ∞:

$$U'_m = -\int_{r_0}^{\infty} qsa\, dr/r^6 \tag{9.23}$$

where q = number of molecules per unit volume;
s = area of the segment of a sphere having radius r which is within the plate;
a = constant.

As we know, the surface of a spherical segment is

$$s = 2\pi r\,(r - r_0)$$

In substituting the value of s in Eq. (9.23) and integrating, we obtain

$$U'_m = -2\pi qa \int_{r_0}^{\infty} \frac{(r - r_0)}{r^5}\, dr = -\frac{\pi qa}{6r_0^3} \tag{9.24}$$

To make the transition from a molecule to unit area of a layer having a thickness of dr_0, the value of U'_m should be multiplied by $q\, dr_0$. The energy of attraction of both plates (per unit area) will be

$$U_m = -\int_{h}^{\infty} qU'_m\, dr_0 = -\frac{\pi}{12}\frac{q^2a}{h^2} \tag{9.25}$$

The attractive force per unit area will then be

$$F_m = -\frac{\partial U_m}{\partial h} = -\frac{\pi}{6}\frac{q^2a}{h^3} = -\frac{A}{6\pi h^3} \tag{9.26}$$

where A is the Hamaker constant.

After measuring the attractive force of the plates for small distances, the constant a and the Hamaker constant can be determined:

$$A = \pi^2 q^2 a \tag{9.27}$$

The value of F_m (taken with a negative sign) expresses the component of disjoining pressure Π_m which depends on molecular attraction.

The force F_m was first measured by Deryagin and Abrikosova in 1953-1954. Their measurements were later confirmed by the English worker J. Kitchener and the Dutch scientists M. Sparnaay, J. Overbeek and de Jong. It was found in the first measurements made by Deryagin and Abrikosova that the attractive forces at distances greater than 300 A between plates were less than expected from the values of a, and that they decreased with distance more rapidly than according to theory.

This prompted the Soviet scientist E. Lifshits to reconsider a theory for the attraction of bodies consisting of many molecules. According to him, in all the media there exist electromagnetic fields randomly fluctuating with time. They propagate as waves, including those in the visible and ultraviolet regions, penetrate into neighbouring bodies, and interact with their molecules. This interaction is what creates the forces of attraction between two bodies when the gap separating them is narrow enough. The corollaries of the theory will be expounded below without presenting complicated calculations based on quantum mechanics.

The theory of Lifschits shows that when molecules are arranged compactly, as in solids and liquids, the energy of interaction cannot be calculated by simply summing up the energies of interaction between molecule pairs because molecular interactions are not additive. Nevertheless, the force of attraction between two plates depends on the distance h as has been shown in Eq. (9.26), but here the constant A gets a different expression. Lifshits connected the value of this constant with the optical properties of bodies.

Eq. (9.26) is valid only for interplate distances below 200 Å. When distances are longer, account should be taken of electromagnetic retardation which is due to the electromagnetic nature of molecular forces predicted by the Russian physicist P. Lebedev. Owing to this nature, the molecular forces propagate not instantaneously, but at the velocity of light. As a result of electromagnetic retardation at distances greater than 300 Å, the attractive force changes according to

$$F_m = -B/h^4 \tag{9.28}$$

To theoretically determine the constant B, it is enough to know the dielectric permittivities of the bodies.*

* This formula was given earlier for metals by H. Casimir and D. Polder.

D. Tabor and other scientists measured the attractive forces fo solids when the width of the gap reached 50 Å; for a small width of the gap, a dependence was discovered to be in accordance with Eq. (9.26) which expresses molecular attraction when electromagnetic retardation is absent. For most solids and liquids, the values of the constant A are within the range of 10^{-14}-10^{-12} erg.

The interaction between surfaces separated by a liquid interlayer or, in other words, the disjoining pressure of the liquid interlayer is of great interest to colloid chemistry. Eqs. (9.26) and (9.28) are applicable in this more general case, the constants A and B depending on the properties of the two bodies as well as of the liquid interlayer. This interlayer may not only reduce surface attraction, but also transform attraction into repulsion. In other words, the molecular or the van der Waals component Π_m of the disjoining pressure of a liquid interlayer can be either negative or positive. The latter case is observed most frequently for a wetting film which separates a gas bubble from a solid support although here we cannot speak of interaction between two bodies through a liquid interlayer. Therefore, disjoining pressure is a broader concept than the interaction of bodies. Equation

$$\Pi_m = -\frac{A}{6\pi h^3}$$

is well applicable to films which are not too thick.

Repulsive forces. Besides the molecular component of disjoining pressure, account should be taken also of its other components. Among them, the repulsive force is of the most general importance and has been studied best of all; it is engendered by the overlapping of the diffuse double ionic layers which are formed in an electrolytic solution at the interface with a foreign phase.

The method of calculating this component was first worked out and applied by B. Deryagin, and it was improved later together with L. Landau. Afterwards, similar calculations were published by I. Langmuir, A. Frumkin, P. Bergmann, P. Löw-Beer, and H. Zocher. Let us expound the principles of these calculations for a simpler case when the surfaces of interacting phases are charged to a value of the potential φ_0.

Let us consider the distribution of the electric potential φ between the surfaces of the plates which have potential φ_0 and are immersed in a solution of a strong (completely dissociated) binary electrolyte. Suppose the coordinate origin is in the centre of a liquid interlayer having a thickness of $2x_0$, and the abscissa is normal to the plate surfaces.

If a surface charged to potential φ_0 borders on an electrolytic solution, the distribution of the potential in a double ionic layer

being formed is described by the equation

$$\varphi = \varphi_0 e^{-\varkappa l} \tag{9.29}$$

where $\varkappa$ = reciprocal of the effective thickness of the electric double layer;
l = distance from the plate surface.

According to this equation, φ is equal to φ_0 at $l = 0$, and $\varphi = 0$ at $l \to \infty$.

When two double ionic layers overlap in the interlayer of the electrolytic solution, the integral of the equation $d^2\varphi/dx^2 = \varkappa^2\varphi$ will be

$$\varphi = \varphi_0 \left(\frac{e^{\varkappa x} + e^{-\varkappa x}}{e^{\varkappa x_0} + e^{-\varkappa x_0}} \right) \tag{9.30}$$

where the coordinate x is counted off from the plane located in the middle of the surfaces of the two plates.

According to Eq. (9.30), the electric potential, while satisfying the relation $d^2\varphi/dx^2 = \varkappa^2\varphi$, assumes the value of φ_0 at $x = \pm x_0$.

To find the electrostatic force of repulsion between plates (being equal to the corresponding component of the disjoining pressure of the interlayer Π_e), Deryagin calculated the difference in the values of Maxwellian and hydrostatic pressure that were applied to the inner and outer surfaces of each plate.

This difference is

$$-\Pi_e = \frac{\varepsilon}{8\pi}(H_1^2 - H_0^2) - (p_1 - p_0) \tag{9.31}$$

where ε = dielectric constant of a liquid interlayer;
H_1 and H_0 = electric field intensity at the inner and outer surfaces of a plate;
p_1 and p_0 = respective hydrostatic pressures.

According to Pascal's law, hydrostatic pressure at all points of a liquid at rest is the same when external forces are absent. In the given case, electric field engendered by charges acts at these points of a double ionic layer. This causes a change in hydrostatic pressure, and its value at a certain point of a liquid interlayer, in comparison with uniform pressure in the electrolyte volume, is determined by the value of the electric potential at this point. Therefore, $p_1 = p_0$ if the potential on the inner surfaces of the plates equals that on the outer ones.

The expression $p_1 = p_0$ should be supplemented with two terms: one electrostriction term supplements the Maxwell expressions for the electric field intensity and another electrostriction term changes the distribution of hydrostatic pressure, particularly, pressure on plates. However, as we know from the theory of electricity, the two

effects have opposite signs, and therefore they compensate one another. However, when account is taken of the electrostriction terms, excess hydrostatic pressure on the median plane ($x = 0$) between the plates where $H = 0$ is not equal to Π_e according to Eq. (9.31). Consequently, the determination of Π_e according to Langmuir produces a result which coincides with Eq. (9.31) only when the electrostriction terms are neglected.

If we suppose that $H = -\partial\varphi/\partial x$ and use Eqs. (9.29) and (9.30) at $l = 0$ and $x = x_0$, we find

$$H_0 = \varkappa\varphi_0 \tag{9.32}$$

and

$$H_1 = \varkappa\varphi_0 \frac{e^{\varkappa x_0} - e^{-\varkappa x_0}}{e^{\varkappa x_0} + e^{-\varkappa x_0}} \tag{9.33}$$

Substituting the values of H_0 and H_1 in Eq. (9.31), we obtain

$$\Pi_e = \frac{\varepsilon}{8\pi}\varkappa^2\varphi_0^2 \frac{4}{(e^{\varkappa x_0} + e^{-\varkappa x_0})^2} \tag{9.34}$$

The repulsive force (the electrostatic component of disjoining pressure) originates when ionic layers overlap; it is proportional to the square of the potential φ_0 on the plate surfaces and rapidly diminishes when the interplate distance exceeds the effective thickness of double ionic layers.

The calculation of pressure Π_e is complicated when the potential φ_0 grows and breaks the condition of the smallness of the dimensionless potential

$$\Omega = \frac{ze\varphi_0}{kT} \tag{9.35}$$

where z = ion valency;
e = electron charge.

As Ω grows, the electrostatic component of disjoining pressure increases tending to the finite limit. This phenomenon, though hardly understandable at first glance, occurs because, according to Boltzmann's theory, the concentration of counterions rapidly grows in proportion to the exponent e^{Ω}, due to the attraction of charges of opposite sign, near the charged surface as its potential φ_0 increases. Consequently, the action of the charged surface becomes screened and, as the distance from it increases, the potential φ rapidly assumes moderate values which do not increase with a further growth in φ_0.

It is rather easy to see how the pressure Π_e changes in a liquid interlayer having a thickness of $2x_0$ in which the potential sharply drops with an increase in the distance from the charged surfaces, but the value of Ω at all points of the interlayer remains sufficiently

high:

$$\Pi_e = \frac{\pi}{8} \varepsilon \left(\frac{kT}{ze}\right)^2 \frac{1}{x_0^2} \tag{9.36}$$

At low values of the dimensionless potential $\Omega = ze\varphi_0/(kT)$, obtained for high values of $\varkappa x_0$, the pressure Π_e diminishes in proportion to the exponent $e^{-2\varkappa x_0}$.

In adding the component of disjoining pressure Π_m, which depends on molecular forces and has a negative sign, and the component of disjoining pressure Π_e, which depends on the overlap of the ionic layers and has a positive sign, we obtain the total disjoining pressure between plates having lyophobic surfaces which do not interact strongly with the dispersion medium. If the plates have lyophilic surfaces, the strong interaction with a liquid may yield a third, structural component of the disjoining pressure of the liquid layers whose structure is changed under the action of the lyophilic surface. This component has not yet been studied well enough quantitatively, and we will not consider it here.

Hitherto, we considered the interaction of similar surfaces. Things are considerably more complicated when a liquid interlayer separates the surfaces of two different bodies. In this case, even if the electric potentials of the surfaces have the same sign, repulsion at sufficiently close distances changes for attraction; this happens the earlier, the greater is the difference in potentials. When the interlayer becomes much thinner than the electric double layer ($1/\varkappa$), the attractive force ($-\Pi_e$) is

$$-\Pi_e = \frac{\varepsilon}{8\pi} \left(\frac{\varphi_2 - \varphi_1}{h}\right)^2 \tag{9.37}$$

where φ_2 and φ_1 are the potentials of both surfaces.

When surfaces bear charges of opposite sign, attraction will be observed at any (but not too great) distances between surfaces.

The negative molecular component of disjoining pressure (being equal to the van der Waals force of attraction) may become positive for heterogeneous surfaces. Thus, both components of disjoining pressure may have either different or the same signs. The latter case is often observed for wetting liquids whose molecular component is positive just as the electrostatic component.

In returning to our consideration of a thin liquid layer which has a thickness of $2x_0$ and is located between identical plates, let us graphically illustrate the energy of interaction $U_m + U_e$, calculated with strict regard to theory when the potential φ_0 is constantly equal to 100 mV, as a function of the half-thickness of the layer x_0 (Fig. 9.5). The curves shown relate to different values of the concentration of an electrolytic solution. When the electrolyte concentration is low (curve *1*), repulsion predominates at almost all the values of the layer thickness, and resultant attraction is observed

only at low values of the thickness; this attraction reaches the maximum at a certain small thickness. When the electrolyte concentration is intermediate (curve *2*), the potential barrier shifts to the left and becomes steeper, narrower, and higher; in this case, a potential hole of little depth is observed when the interlayer is thick. When the electrolyte concentration is sufficiently high (curve *3*), the region of the thickness at which repulsion is observed shifts to the left even

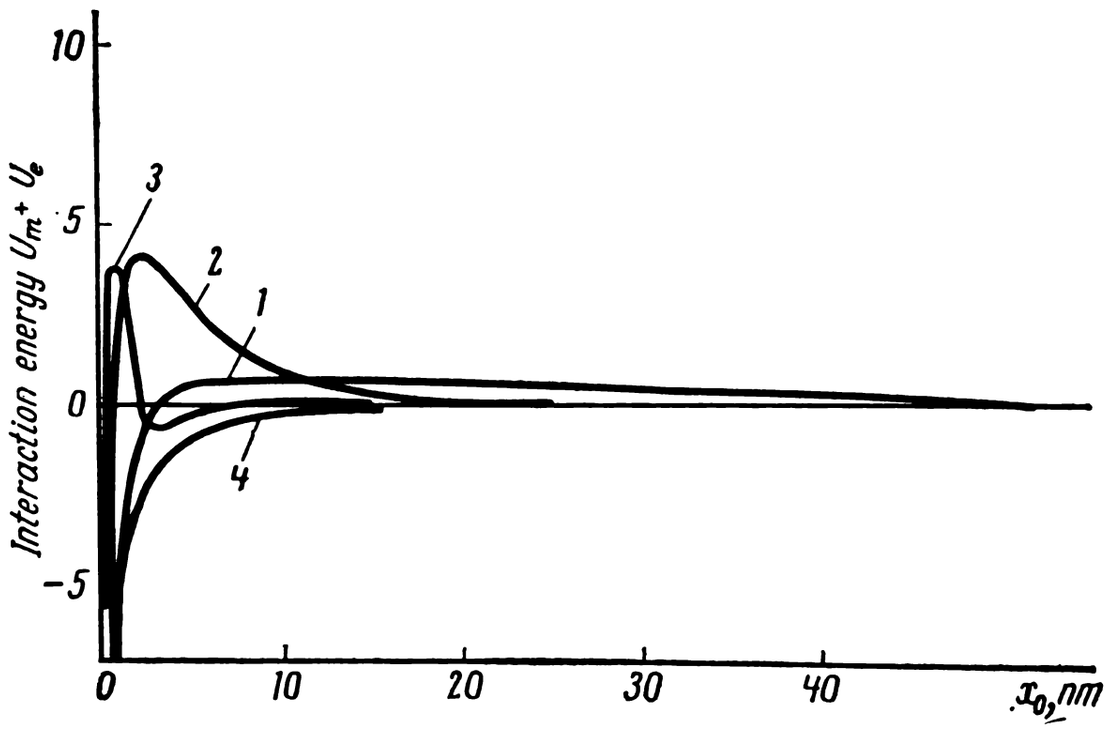

Fig. 9.5. Energy of interaction, $U_m + U_e$, between plates as a function of the half-thickness of the liquid interlayer x_0.
$A = 10^{-12}$ erg; $\varphi_0 = 100$ mV; values of $\varkappa$: *1*—10^5, *2*—10^6, *3*—10^7, *4*—$10^{7.5}$ cm^{-1}

more and narrows down while the right-hand potential hole becomes deeper. Lastly, when the concentration is even higher (curve *4*), the barrier disappears and both potential holes merge.

Hitherto, we have discussed interaction of plates. Such cases are realized in colloidal systems whose particles are flat, and also in some clayey minerals on their intracrystalline swelling. For instance, when a montmorillonite crystal saturated with ions of lithium or sodium is put into a dilute sodium chloride solution, the distance between layers which constitute its lattice increases and the crystal becomes larger. The thickness of the interlayers of a NaCl solution implanted between the reticular crystal planes can reach 300 Å. Thus, the disjoining pressure of interlayers is involved in the swelling of montmorillonite crystals.

Theoretically, swelling is the greater, the less is the concentration of an electrolytic solution; the process ends when the concentration of a monovalent symmetric electrolyte reaches a certain limit, say of the order of 0.1M. However, colloidal systems having more or less spherical particles are more commonly encountered in nature

and technological processes. The interaction (e.g., the force of repulsion F) between two spherical particles having radius r at a close distance h_0 can be calculated approximately by the formula

$$F = \pi r \int_{h_0}^{\infty} \Pi \, dh \tag{9.38}$$

where Π is disjoining pressure between flat identical particles which are separated by an interlayer of the same liquid having a thickness of h.

Eq. (9.38) and the formulas for calculating Π_m and Π_e can be used to plot potential curves, similar to those represented in Fig. 9.5, for the energy of interaction between spherical lyophobic particles in electrolytic solutions.

The shape of the curves changes likewise with the electrolyte concentration. Thus, in using the diagrams given above, the aggregative stability of colloidal systems can be studied by considering the balance between forces of molecular attraction and electrostatic repulsion.

We have discussed above the interaction between two surfaces on the basis of the concepts of disjoining pressure. However, this interaction can be interpreted in terms of the energies (or forces) acting between two charged parallel flat surfaces which are separated by a narrow gap.

Let us briefly consider, without resorting to rather complicated mathematical operations*, the final conclusions that can be drawn by taking into account the energy of interaction U_e between two smooth plates which bear a charge of the same sign and are at a very small distance away from one another. This energy per square centimetre of the surface can be expressed by the equation

$$U_e = \frac{64cRT}{\varkappa} \gamma^2 e^{-2\varkappa x_0}$$

where

$$\gamma = \frac{\exp(zF\varphi_0/2RT) - 1}{\exp(zF\varphi_0/2RT) + 1}$$

The energy of attraction U_m, caused by the action of molecular forces between the plates and related to a square centimetre of the surface, is expressed by the equation

$$U_m = -\frac{A}{12\pi (2x_0)^2}$$

where A = Hamaker constant;
$2x_0$ = interplate distance.

* The appropriate mathematical treatment is given in: A. Sheludko, *Kolloidna khimiya* (Colloid Chemistry), Nauka i Izkustvo, Sofia, 1957.

The energies U_e and U_m are opposite in sign because repulsion occurs in the first case, and attraction, in the second. Thus, the total energy of interaction of two plates per square centimetre of the surface will be

$$U = \frac{64cRT}{\varkappa}\gamma^2 e^{-2\varkappa x_0} - \frac{A}{48\pi x_0^2}$$

This equation does not take account of the structural component of the disjoining pressure of liquid layers whose properties have been changed under the action of the surfaces.

3. CHANGE IN THE ENERGY OF INTERACTION BETWEEN MICELLES AS THEY APPROACH ONE ANOTHER

Proceeding from the material expounded in the last section, we can imagine how the energy of interaction between two colloidal particles bearing a charge of the same sign changes as they approach one another; this energy is the result of the addition of the molecular

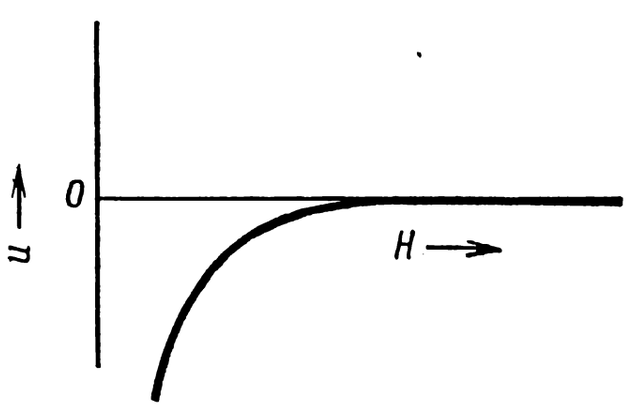

Fig. 9.6. Potential curve for particles in vacuum, in a gas or in a liquid which does not contain stabilizing ions

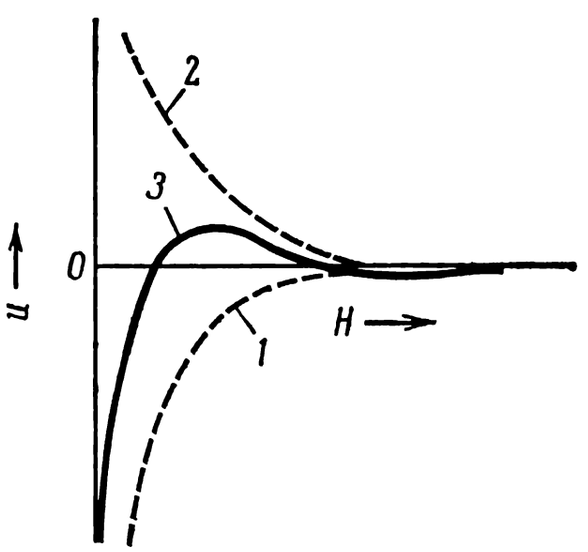

Fig. 9.7. Potential curves for particles in an ordinary lyosol stabilized with ions:

1—change in the energy of molecular attraction; *2*—change in the energy of electrostatic repulsion; *3*—resultant potential curve

forces of attraction and the electrostatic forces of repulsion. To this end, let us consider the potential curves (Figs. 9.6 and 9.7) for the energy of interaction between two approaching particles (the energy of repulsion is plotted above zero, and the energy of attraction, below it) as a function of distance H between particles.

Fig. 9.6 presents a potential curve for particles in vacuum, in a gas or in a liquid which does not contain stabilizing ions and does not form a solvate shell. The left-hand part of the curve shows that,

at low values of H, the energy of molecular interaction changes in inverse proportion to squared distance. At the right-hand part of the curve at rather high values of H, the energy of molecular attraction changes in inverse proportion to cubed distance owing to electromagnetic retardation. The location of the curve below the abscissa indicates that the particles which have approached one another should stick together when a stabilizer is absent. In reality, this corresponds to two particles of an aerosol or to two completely astabilized particles of a lyosol. The rate of coagulation of such systems is determined only by the time needed for particles in Brownian motion to approach one another.

Fig. 9.7 presents curves for approaching micelles of an ordinary ion-stabilized lyosol whose particles bear an electric double layer. Here, the picture is much more complicated. Curve *1* characterizes a change in the energy of molecular attraction between particles, and it is similar to the curve in Fig. 9.6. Curve *2* characterizes a change in the energy of electric repulsion between the electric double layers of particles, and therefore it is situated above the abscissa.

Curve *3* is the resultant potential curve plotted on the basis of the first two curves by geometrically adding up their ordinates. At great distances between particles, the resultant curve lies below the abscissa (the secondary potential hole of little depth or the long-range potential minimum *). The forces of molecular attraction somewhat predominate between particles because these forces diminish according to the power law whereas the forces of electrostatic repulsion decrease according to the exponential law. At average distances which correspond to the thickness of effective ionic shells (about 100 nm), the curve is above the abscissa and forms an energy barrier. Thus, the forces of electrostatic repulsion prevail at this distance. Attractive forces predominate again at closer distances, and this segment of the curve is below the abscissa (the primary potential hole or the short-range potential minimum). For particles incapable of sticking together, the primary minimum is engendered as the molecular forces of attraction are compensated by the Born repulsion.

The shape of the resultant potential curve can explain several phenomena which are observed when colloidal systems astabilize and coagulate

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* The interaction of particles at great distances, characterized by the presence of a negative minimum of little depth on the potential curve, does not have a special name. Various terms have been suggested: long-range coagulation, coagulation in the secondary minimum, long-range aggregation, and flocculation. We will use all these terms except the latter because it is purely descriptive (the formation of flakes, flocculi) and does not specify whether flocculation occurs as a result of true coagulation or long-range aggregation. The term "coagulation" will be applied to all types of particle aggregation, from coalescence to long-range aggregation. "True coagulation" will imply direct physical contact between particles.

The negative minimum of energy, which corresponds to rather great distances between particles and is a potential hole of very little depth, explains thixotropy, i.e., the conversion of gels into sols on stirring and the subsequent transition of sols to gels when a system is allowed to stand. Thixotropy will be dealt with at greater length in Chap. 10. Another phenomenon, which can be interpreted in terms of the existence of a minimum at the right-hand part of the potential curve, is that small particles adhering to a solid wall are capable of undergoing rather intensive Brownian motion near the wall, as was observed by Buzagh under the microscope. Several authors use this minimum on the potential curve to explain the ability of many bacteria and viruses to stay near one another and form chains without contacting one another.

E. Langeland discovered that arrays of small particles moving around large ones are preserved in aqueous dispersions of rubber (latices) which can be attributed only to long-range forces. Other microobjects behave similarly.

The positive maximum (energy barrier) on the curve which corresponds to mean distances is the reason why not all particles stick together as they approach one another in slow coagulation. If the energy barrier is smaller or is at least of the same order as the average kinetic energy of moving particles, the particles will apparently be able to overcome the electrostatic forces of repulsion, approach one another to a very small distance where the molecular forces of attraction prevail, and then stick together. If the energy barrier is high, the particles will not be able to overcome it and to form aggregates. Of course, particles stick together as they approach one another if the thickness of the electric double layer is reduced, for instance, by the addition of an electrolyte to a system, decreasing therefore the repulsive forces so that the energy barrier disappears completely.

The presence of a deep potential hole on the potential curve left of the positive maximum explains the mechanical strength of a coagulate. Particles at close distance are strongly bound with one another by van der Waals forces, and the aggregates formed acquire properties of a solid. The minimum on the potential curve, being located in the region of the negative values of the interaction energy, is apparently engendered when the forces of molecular attraction are counterbalanced by the force of repulsion of electron clouds (the Born repulsion); it corresponds to the physical contact between both particles. This is the most stable state of a system in which it has the least free energy.

Some researchers believe that the surface of particles (mainly lyophilic particles) is often covered with one or several layers of molecules of a dispersion medium which are never pressed out of the gap between colliding particles because the energy of desorption of these molecules is greater than the kinetic energy of moving particles.

The presence of interlayers of a strongly bound medium about 6-10 Å thick prevents particles from approaching one another to a distance at which the energy of molecular attraction becomes very great. This causes a qualitative change in the type of interaction. According to the classical theory, there is always a very deep short-range potential hole, but it is either not deep or absent altogether when an interlayer of a medium is present. In both cases, coagulation may occur only owing to the presence of a long-range potential hole.

The presence of molecules of a medium, which are strongly adsorbed and which are not pressed out in coagulation, on the surface of colloidal particles was also indicated by Rehbinder.

4. SOLVATION OF PARTICLES. STRUCTURAL-MECHANICAL AND ENTROPY FACTORS OF STABILITY

The concepts of the molecular forces of attraction and the electrostatic forces of repulsion are the basis of the modern theory of the stability and coagulation of colloidal systems stabilized with ions. But there are also other causes of the stability of colloidal systems. For example, the stability of colloidal systems having a liquid dispersion medium may be caused by the formation, on the particle surface, of sufficiently developed solvate layers which consist of molecules of the dispersion medium. According to Rehbinder, such layers prevent particles from sticking together because the former can resist shear which hinders their pressing out of the gap between particles; besides, there is no noticeable surface tension at the interface between solvate shells and a free medium. According to Deryagin two solvated particles do not stick together as they approach each other owing to the origination of disjoining pressure which appears because the boundary solvate shells differ in properties from the volume phase.

Solvate shells are formed at the interface. There is no molecular attraction between these shells because the force of interaction between the molecules of a layer is practically equal to that between the molecules of a medium. When particles approach one another, work must be done to remove the solvate shell (desorption work), and this causes the appearance of considerably strong forces of repulsion between particles. Investigations carried out by B. Deryagin, N. Churayev, S. Nerpin, Yu. Popovsky, M. Metsik, G. Zorin, and others confirm the existence of boundary layers with a specific structure.

The formation of sufficiently developed solvate shells is hardly probable for colloidal systems having a lyophobic dispersed phase because of the weak energy interaction between the medium and the dispersed phase. Solvation may occur only when the surface molecu-

les of a dispersed phase are bound to the molecules of a dispersion medium by chemical bonds or, at least, by hydrogen bridges.

Systems whose stability can be attributed to solvation include the hydrosols of SiO_2 and hydroxides of polyvalent metals. These systems do not obey the regularities of the coagulation of lyophobic sols, are reversible to a certain extent, and can exist without a stabilizer; therefore, they are related to lyophilic colloidal systems. However, one must be careful in discussing the cause of the stability of such systems because, as has been shown recently, they are not sols in many cases, but solutions containing macromolecules.

Solvation also seems to considerably affect stability in disperse systems which have a non-polar hydrocarbon medium and are important in the production and utilization of oil products. Such systems, e.g., solutions of surfactants and highly dispersed suspensions in hydrocarbons, have been thoroughly studied by G. Fuchs. The stability of these systems was found to depend on the structure of hydrocarbon molecules, on its conformity to the structure of the molecules of the dispersed phase, on the dielectric constant of the medium, and on the presence of traces of substances having polar and diphilic molecules. As Overbeek has shown, the electric double layer and electrostatic interactions must not be neglected for these systems.

Attempts were made to explain the stability of lyophobic colloidal systems by the induced solvation of their particles. According to these concepts, the aggregative stability of lyophobic sols, being connected with the origination of an electric double layer on particles, is caused by the solvation of counterions of the double layer and, consequently, the creation of a solvate shell around lyophobic particles rather than by the repulsion of particles by electrostatic forces.

The weak points of such an explanation of aggregative stability are apparent. It is very difficult to imagine how continuous solvate shells, preventing the sticking together of particles as they approach one another, can originate around lyophobic particles as a result of the solvation of counterions. Indeed, solvate shells consisting of polar molecules of a medium are formed around each counterion of a double layer. As a result, at the interface of the shells of two neighbouring counterions bearing a charge of the same sign, the dipole molecules of a medium will face one another by their similarly charged ends and, consequently, will undergo mutual repulsion. Moreover, the microstructure of the layer surrounding a particle continuously changes owing to the thermal motion of ions. Of course, under such conditions, the attraction and the orientation of dipoles cannot result in the creation of a continuous layer which consists of coherent ions and molecules of a medium and is needed for ensuring positive disjoining pressure or the elasticity of a solvate shell. Positive disjoining pressure, which causes the aggregative stability of lyophobic

colloids, can originate only as a result of the deformation of ionic atmospheres, i.e., it can be determined only by electrostatic forces.

In addition, the concept that the stability of typical lyophobic colloidal systems stabilized with ions can be determined by solvation does not fit in both with their ability to coagulate under the action of traces of electrolytes and generally with all the regularities of electrolytic coagulation that will be discussed later. Furthermore, if the stability of lyophobic systems is attributed to the solvation of ions, it is not clear how electrokinetic phenomena can occur. To preclude coagulation, the solvate shell around a particle must be sufficiently thick and should in any case extend beyond the micellar slipping plane. However, in this case, a micelle cannot rupture along the slipping plane when an electric field is applied to it. Lastly, the attribution of the stability of colloidal systems to the solvation of counterions of the electric double layer does not explain the mutual coagulation of sols whose particles bear charges of a different sign. But if electrostatic interaction is used to explain the stability and coagulation of colloidal systems, mutual coagulation does not require additional explanation and can be interpreted strictly quantitatively.

A more acceptable view is that the stability of lyophobic colloidal systems is promoted by the solvation of the potential-determining ions. But some aspects are difficult to explain here as well.

It should be thus concluded that solvation can ensure the stability of lyophobic, particularly hydrophobic, colloidal systems only in special cases or can serve as a factor which supplements the action of the electric forces. Even when solvation clearly contributes to the stability of a colloidal system, it is very difficult to take this factor into account because there is no quantitative theory of solvation.

Besides the thermodynamic factors of stability including the electric double layer and the solvate shell around a colloidal particle, the strength of a structural-mechanical barrier which may originate on the particle surface can also affect the stability of colloidal systems. According to Rehbinder, this factor cannot be called a thermodynamic one because a shell, being a structural-mechanical barrier, is not necessarily restored spontaneously when it is eliminated or ruptured. In addition, the shell is not in equilibrium with the surrounding medium.

It has long been held that the stability of foams and emulsions should sharply grow when the interface between the dispersed phase and the dispersion medium has a layer of molecules of a stabilizer possessing elevated structural viscosity or even certain mechanical strength and being, as it were, a structural-mechanical barrier which prevents particles from approaching one another.

The concept of the structural-mechanical factor of stabilization has been evolved to the greatest extent by Rehbinder. According to him, stabilizing properties are displayed by saturated or almost

saturated adsorption layers of the oriented molecules of surfactants which form two-dimensional structures. Colloidal adsorption layers, which are peculiar, film (two-dimensional) gels or lyogels greatly solvated by the dispersion medium and diffusing into the intermicellar liquid, have the strongest stabilizing action. Substances capable of forming such layers are proteins and alkaline soaps in hydrosols; in oleosols, they are resins, soaps of polyvalent metals and lipids.

According to Rehbinder, the gelatinous adsorption layers of a stabilizer have a stabilizing action because the highly viscous interlayer between the particles does not have time to be pressed out during the collision of particles of a dispersed phase which are in Brownian motion or in flow. Under certain conditions, the stabilization of dispersed systems by adsorption-solvate shells, which possess elasticity and mechanical strength, can infinitely increase the stability of a system up to the complete fixation of its particles. An example of this is the solidification of the liquid interlayers between air bubbles of foam owing to gelation or polymerization processes. Rehbinder notes that the formation of a structural-mechanical barrier is enough for stabilization only when the surface energy at the outer boundary of the adsorption layer is small and does not grow sharply nearer a particle. When there is a cross-linked shell which is not lyophilic but lyophobic, particles may stick together as a result of the cohesion of the shells by their outer surfaces. Such phenomena can be observed in flotation when surfactants are adsorbed by polar groups on the surface of solid hydrophilic particles. The hydrocarbon chains facing the aqueous medium are bound with one another by peculiar local sticking together of hydrophobic shells.

According to Rehbinder, the structural-mechanical barrier is the strongest stabilization factor and its utilization seems to be required for obtaining highly stable, especially concentrated dispersed systems such as industrial foams, emulsions, and suspensions.

However, we can apparently speak of the structural-mechanical properties of an adsorption layer only when the molecules of such a stabilizer as soap-like substances or adsorbable polymers are present in a system and can form a two-dimensional gel. It follows that emulsions can be stabilized by the structural-mechanical factor only at sufficiently high concentrations of a stabilizer when compact, well solvated gelatinous layers of high strength are formed at the interface.

G. Martynov believes that the adsorption multilayers of surfactants act in the following way. The molecular forces of attraction are universal, i.e., they act between any bodies. Suppose there are two identical particles whose dispersed phase is denoted by *1* and the polymolecular adsorption layer, by *2* (Fig. 9.8). Apparently, the energy of interaction of the particles will be

$$U_1 \approx k_{1-1}/H^2 \qquad (9.39)$$

where k_{1-1} = constant characterizing the interaction between both particles;
H = interparticle distance.

The energy of interaction of the adsorption layers (films) will be

$$U_2 \approx k_{2-2}/(H-2h)^2 \qquad (9.40)$$

where k_{2-2} = constant characterizing the interaction between the adsorption layers;
h = thickness of the adsorption layer.

As we may see, the regularities of interaction in both cases are qualitatively the same, and only the constants of the interaction and the denominators of the equations change.

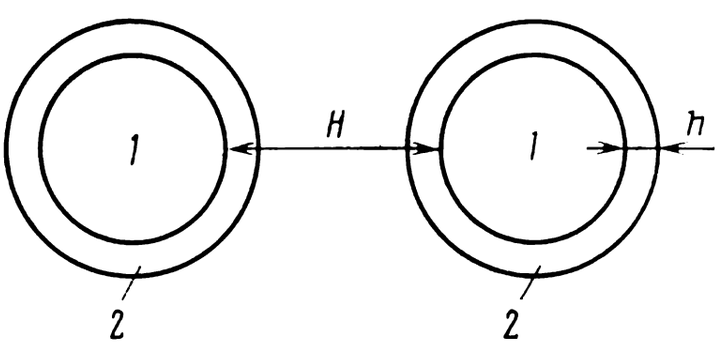

Fig. 9.8. Diagram for the interaction of particles stabilized with surfactant multilayers:
1—particles; *2*—adsorption layer of a surfactant; H—distance between particles; h—thickness of the adsorption layer

At short distances, the contribution of the film to the energy of interaction between particles cannot be neglected, and the energy of attraction of particles will be

$$U = k_{1-1}/H^2 + k_{2-2}/(H-2h)^2 \qquad (9.41)$$

The adsorption layer, being a structural-mechanical barrier, thus affects the interaction between particles without eliminating their attraction. Consequently, adsorption films should not have caused an increase in the stability of a system. But if $k_{2-2} = 0$, the molecular attraction between films can be neglected. At the same time, stabilizing films can be a hindrance to the close approach of particles. If particles cannot approach one another, the molecular forces of attraction between them will be weak because the distance is great. This is what causes an increase in stability.

When the electric double layer is absent, the effectiveness of the stabilizing adsorption films is determined by the following conditions: (1) the stabilizing film should be sufficiently lyophilic, i.e., $k_{2-2} \simeq \simeq 0$, and (2) the longer are the molecules of a substance which forms a protective film, the greater is the distance by which particles can

approach one another and the lower are the molecular forces of attraction between them (i.e., the higher is the stability of a system).

In conclusion, let us consider the concepts of the entropy factor of stability.

It was shown in the works of R. Simha, F. Eirich, and many other researchers that sufficiently long and flexible molecules of surfactants and polymers can adsorb on the surface of a solid by their individual units. In this case, many ends of chains or loops formed by adsorbed

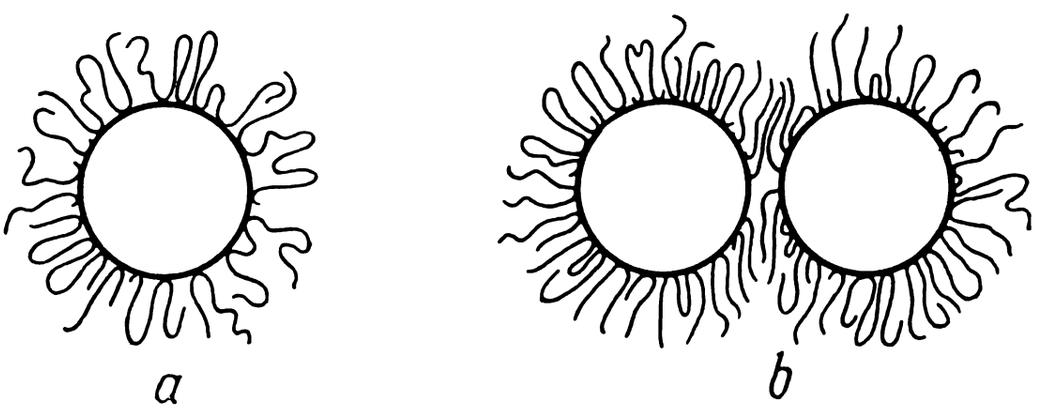

Fig. 9.9. Schematic illustration of colloidal particles which have adsorbed individual units of macromolecular chains in micro-Brownian motion:
a—particle; *b*—two particles which have approached one another

molecules are in the dispersion medium and can undergo micro-Brownian motion (Fig. 9.9*a*), thus stabilizing a system. According to Oberbeek, colloidal particles are stabilized here by the mutual repulsion of flexible regions of molecular chains which protrude into the medium.

According to another viewpoint, the number of conformations realized by flexible chains of a stabilizer diminishes as particles having individual units of macromolecules adsorbed on their surface approach one another (Fig. 9.9*b*). Such a diminution in the number of conformations, caused by the "crowdedness" of macromolecules between the approached particles, decreases the entropy and, consequently, increases the free energy of a system. Of course, this will stabilize colloidal particles, i.e., increase the aggregative stability of a system.

The third explanation of the stabilizing action of partially adsorbed macromolecules was offered by A. Bromberg back in 1946. According to him, stabilization in this case is determined by the osmotic forces which act in the adsorption layers. D. Napper also noted that the osmotic forces appear when the layers of the partially free macromolecules overlap. Thus, a change in the entropy of polymer molecules, which are in the gap between approaching surfaces, should cause an inflow of a liquid from the solution volume into the gap and engender disjoining pressure which stabilizes a system.

5. RULES OF COAGULATION BY ELECTROLYTES

Colloidal systems may coagulate under the action of several factors: the aging of a system, a change in the concentration of a dispersed phase or in temperature, mechanical effects, the action of light, and so forth. However, coagulation which occurs when electrolytes are added is of the greatest theoretical and practical importance. In this textbook, we will deal at length with coagulation by electrolytes and will only briefly touch on other causes of coagulation.

The ability of colloidal solutions stabilized with ions to coagulate under the action of electrolytes was noted by the first investigators of colloidal systems: F. Selmi, Th. Graham, and I. Borshchov. They found that all electrolytes are capable of causing coagulation. As subsequent investigations have shown, stabilizing electrolytes are not an exception in this respect, but their concentration in a system must be sufficiently high to compress the electric double layer and to lower the energy barrier hindering the sticking together of particles when they collide.

Hardy found in 1900 that not all the ions of an electrolyte have a coagulating effect, but only those bearing a charge of the same sign as that of the counterion of a micelle (or, what is the same, a charge which is opposite in sign to that of a colloidal particle). Thus, cations coagulate sols having negatively charged particles, and anions, sols having positively charged particles.

It was also shown that a certain minimum concentration of an electrolyte in a sol must be reached for coagulation to begin. This quantity γ, which is known as the *coagulation threshold* and is usually expressed in mmol/l or mg-equiv/l, apparently corresponds to the compression of the electric double layer until it is no longer the energy barrier which protects particles from sticking together by means of the molecular forces of attraction. The coagulation thresholds for the arsenic sulphide sol having negatively charged particles by some electrolytes are given below (according to H. Freundlich).

Electrolyte	γ, mmol/l	Electrolyte	γ, mmol/l
CH_3COOK	110.0	$BaCl_2$	0.69
LiCl	58.0	$ZnCl_2$	0.68
NaCl	51.0	$CaCl_2$	0.65
KNO_3	50.0	$UO_2(NO_3)_2$	0.64
KCl	49.5	$SrCl_2$	0.63
HCl	31.0	$Al(NO_3)_3$	0.095
$MgSO_4$	0.81	$AlCl_3$	0.093
$MgCl_2$	0.71	$Ce(NO_3)_3$	0.080

The beginning of coagulation can be determined by various signs: a change in sol colour, the appearance of turbidity, the commencement of precipitation of the dispersed phase, and so forth. The appearance of these signs does not always coincide in time. Moreover, the coagulation threshold depends to a certain extent on sol concentration and is therefore a relative characteristic of sol stability with respect to a given electrolyte. In any case, it is always necessary to precisely indicate the conditions under which the coagulation threshold of a sol was being determined.

As early as 1882, H. Schulze found that the coagulating power of an ion is the greater, the higher is its valency. This dependence was confirmed by W. Hardy and became known as the rule of Schulze and Hardy or the *valency rule*. The rule does not mean direct proportionality between the valency of an ion and its coagulating action; the coagulating power grows much more rapidly than valency. For the As_2S_3 sol, Schulze found the ratio of the coagulating power of mono-, di-, and trivalent cations to be 1:20:350; for the same sol and the same cations, Freundlich found the ratio 1:7:531. H. Picton and S. Linder determined the ratio as being 1:20:1500. The discrepancy between the values of coagulation thresholds found by various authors is due to the difficulty in obtaining a colloidal system of the same characteristics and to the fact that conditions were not identical when the thresholds were being determined.

Further experiments have shown that the coagulating power of ions of the same valency grows with the ionic radius. In other words, cations or anions of the same valency are arranged in an ordinary lyotropic series by their coagulating action. For monovalent cations and negatively charged particles of a silver iodide sol, such a regularity is seen from the following data (according to L. Lepin and A. Bromberg).

Electrolyte	γ, mg-equiv/l	Electrolyte	γ, mg-equiv/l
LiCl	582	Li_2SO_4	640
NaCl	300	Na_2SO_4	420
KCl	255	K_2SO_4	272
$LiNO_3$	600		
$NaNO_3$	360		
KNO_3	260		

A change in the coagulating action in the lyotropic series of ions of alkaline-earth metals is expressed less than that in the series of monovalent cations. A change in the coagulating action of anions in the lyotropic series is less pronounced when sols having positively charged particles are coagulated by anions.

The coagulating action of organic ions is remarkable. The positively charged monovalent ions of alkaloids and dyes act much more

strongly than the inorganic electrolyte ions of the same valency. This is due to the great adsorbability of bulky organic ions which are better polarized.

Hardy believed that coagulation should begin at the isoelectric point when the ζ-potential of particles is equal to zero. But it was found later that coagulation usually begins not at the isoelectric point, but as soon as a certain critical ζ-potential is reached. The value of the critical ζ-potential turned out to depend little on the type of the electrolyte by means of which it was reached. For many systems, this potential is close to 30 mV, as can be seen in Table 9.1.

Table 9.1. **Values of the Critical Potential ζ_{crit} for the As_2S_3 Sol (according to F. Powis) and the Fe_2O_3 Sol (according to S. Gosh)**

Sol	Coagulating electrolyte	Electrolyte concentration, mg-equiv/l	ζ_{crit}, mV
As_2S_3 sol (negatively charged particles)	KCl	40.0	44
	$BaCl_2$	1.0	26
	$AlCl_3$	0.15	25
	$Th(NO_3)_4$	0.20	27
Fe_2O_3 sol (positively charged particles)	KCl	100.0	34
	NaOH	7.5	31
	K_2SO_4	6.6	32
	K_2CrO_4	6.5	32
	$K_3Fe(CN)_6$	0.65	30

However, in many cases, the value of the critical ζ-potential, which corresponds to the beginning of coagulation, greatly differs from 30 mV. Sometimes, as the ζ-potential diminishes, sols not only do not coagulate, but even increase their stability; conversely, a growth in the potential is occasionally accompanied by coagulation. This indicates that the relationship between the ζ-potential and stability is more complicated than some investigators were inclined to believe. However, the electrokinetic potential has been determined so far without taking account of electrophoretic retardation, electric relaxation, and other factors; therefore, the values of the critical potential so found are inaccurate in many cases.

Several workers have found that the precipitate consisting of the coagulated dispersed phase of a colloidal system always contains the coagulating ions because, in coagulation, some counterions of sol micelles are exchanged with the coagulating ions of an electrolyte with which coagulation is being effected.

6. THEORIES OF COAGULATION BY ELECTROLYTES

The foregoing rules of the coagulation of sols cover, in the main, all its characteristics. Let us now see how the phenomena observed in coagulation by electrolytes can be interpreted.

Various authors had proposed several theories of coagulation by electrolytes. They include the chemical theory of coagulation (J. Duclaux), the adsorption theory (H. Freundlich), and the electrostatic theory (H. Müller, A. Rabinovich, V. Kargin). However, they all lost their importance for one reason or another and are now only of historic interest. The physical theory of coagulation by electrolytes is now generally accepted, being based on the general principles of statistical physics, the theory of solutions, and the theory of molecular forces. The physical theory of coagulation by electrolytes is based on the consideration of the balance between the molecular forces of attraction and the ionic forces of electrostatic repulsion that act between particles, as was exemplified by the interaction of plate-like particles in the second section of this chapter.

A qualitative approach to the study of sol stability was initiated by H. Kallmann and M. Willstätter in 1932. The first quantitative calculations were made by Deryagin in the late 1930's and were completed by him and Landau in 1941. A similar approach to the study of the stability of colloidal systems was later developed by the Dutch investigators Verwey and Overbeek. The physical theory of coagulation is now often called the DLVO theory, the letters standing for the initial letters of the names of its main authors.

In considering the coagulation of colloidal systems, a distinction should be made between two extreme cases:

(1) neutralization coagulation when stability is lost as a result of the discharge of colloidal particles and a diminution in their φ_0-potential*;

(2) concentration coagulation when the loss of stability is caused by the compression of the diffuse double layer rather than by a drop in the φ_0-potential.

Let us consider these two types of coagulation in greater detail.

Neutralization coagulation. This type of coagulation is observed for sols with weakly charged particles which have comparatively low values of the φ_0-potential. In this case, sols usually coagulate as the electric charge of particles diminishes owing to a decrease

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* According to specified concepts, the intensity of the repulsive forces is determined not by the potential φ_0, but by the potential φ_δ which corresponds to the boundary of the Stern layer. An important fact is that $\varphi_\delta < \varphi_0$.

in the adsorption of potential-determining ions. As the charge diminishes, the electric forces of repulsion between particles weaken, particles stick together as they approach one another, and precipitate.

The theory evolved by Deryagin makes it possible to calculate the lowest value of the φ_0-potential at which the energy barrier should disappear, i.e., when the resultant potential curve (Fig. 9.10)

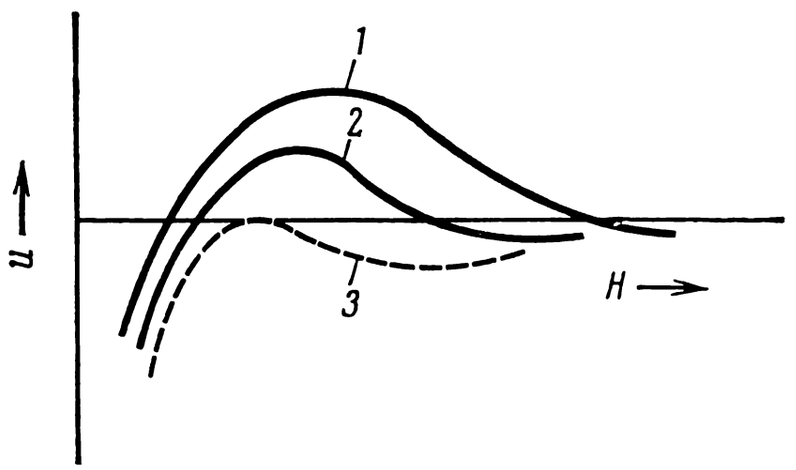

Fig. 9.10. Potential curves characterizing a change in the interaction energy of two colloidal particles as a function of the distance H between their surfaces. The numeration of the curves grows as the potential diminishes

characterizing the dependence of the energy of interaction between particles on the distance between them should touch the abscissa at a single point (the dashed curve). At a sufficiently low φ_0-potential, the relationship between the critical potential $\varphi_{0,crit}$, at which the energy barrier disappears, and the thickness $1/\varkappa$ (or h) of diffuse layers, which surround both colloidal particles, is expressed by the equation

$$\varphi_{0,\,crit} = \sqrt{C\frac{A}{\varepsilon \cdot 1/\varkappa}} = \sqrt{C\frac{A\varkappa}{\varepsilon}} \qquad (9.42)$$

where C = constant;
A = attraction constant;
ε = dielectric constant of a solution.

The relationship between $\varphi_{0,crit}$ and $\varkappa$ which follows from Eq. (9.42) has been empirically found by H. Eilers and J. Korff as early as 1936. According to them and to Eq. (9.42)

$$\varphi_0^2 h = \varphi_0^2 \cdot 1/\varkappa = C\frac{A}{\varepsilon} \gtrless B \qquad (9.43)$$

where B is a certain critical quantity determined experimentally.

If $\varphi_0^2 h < B$, this is a prerequisite for coagulation; if $\varphi_0^2 h > B$, a system is stable.

For sufficiently diluted electrolytic solutions when the diffuse layer is very thick, and for low values of the φ_0-potential, it can be taken that the potential is rather close to the ζ-potential which

is measured by the mobility of particles in the electric field (Fig. 9.11*a*). However, the total jump in the φ_0-potential or the Stern φ_δ-potential, which corresponds to the boundary between the ionic condenser and the diffuse layer, should not, strictly speaking, be identified with the ζ-potential because this can occasionally produce incorrect results. Indeed, the determination of the ζ-potential is connected with the hydrodynamic characteristics of a system, i.e., with the

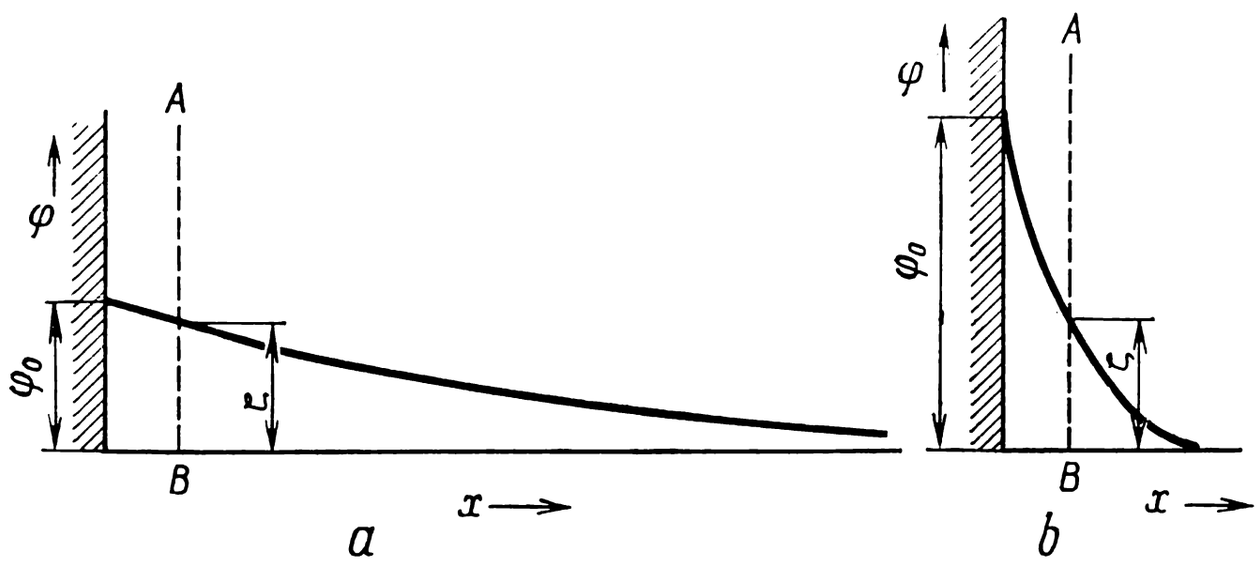

Fig. 9.11. Dependence of the φ_0- and ζ-potentials for weakly charged particles in a diluted electrolytic solution (*a*) and for strongly charged particles in a sufficiently concentrated electrolytic solution (*b*)

position of the slipping plane at the particle—solution interface or with the viscosity of the liquid layers adjacent to it, whereas φ_0- and φ_δ-potentials are apparently not related to these characteristics. The ζ-potential is used as the criterion of stability of colloidal systems because it can be easily measured experimentally and its change under definite conditions is similar to that in the φ_0-potential.

Concentration coagulation. This type of coagulation is usually observed for sols having highly charged particles as the concentration of an indifferent electrolyte in a system increases. This circumstance makes it possible, as the first approximation, to take no account of a possible change in the φ_0-potential when various adsorption or desorption phenomena occur. According to the DLVO theory, a system coagulates here owing only to the electrostatic effect of the compression of the electric double layer.

In the extreme case, the surface potential, or the φ_0-potential, can retain rather high values (more than 100 mV) in coagulation. There is then no longer any correlation between the ζ-potential, which may drop considerably as the concentration of the electrolytic solution increases, and the φ_0-potential (see Fig. 9.11*b*). There is

no relationship now between the stability of a system and the φ_0- and ζ-potentials. Thus, it becomes clear why the ζ-potential can far from always be a criterion of sol stability.

To understand the mechanism of concentration coagulation, it is necessary to discuss the dependence of the forces of electrostatic interaction on the φ_0-potential, being exemplified earlier by two plates. Theoretically, as the φ_0-potential of both surfaces grows infinitely, the force of electrostatic repulsion F_e between colloidal

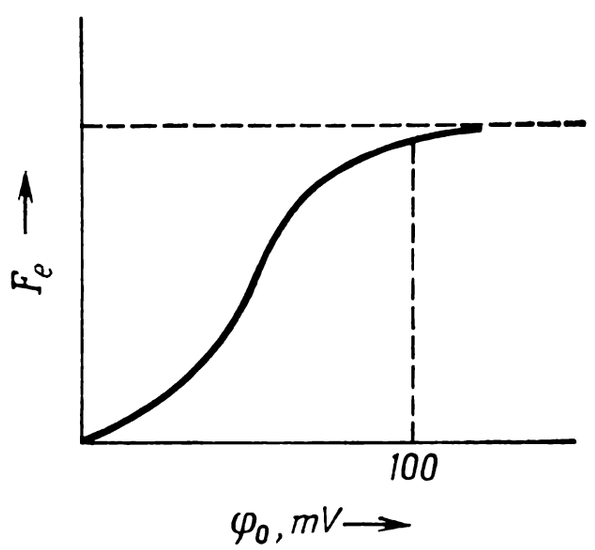

Fig. 9.12. Dependence of the electrostatic repulsive force F_e between two colloidal particles on the φ_0-potential of their surface

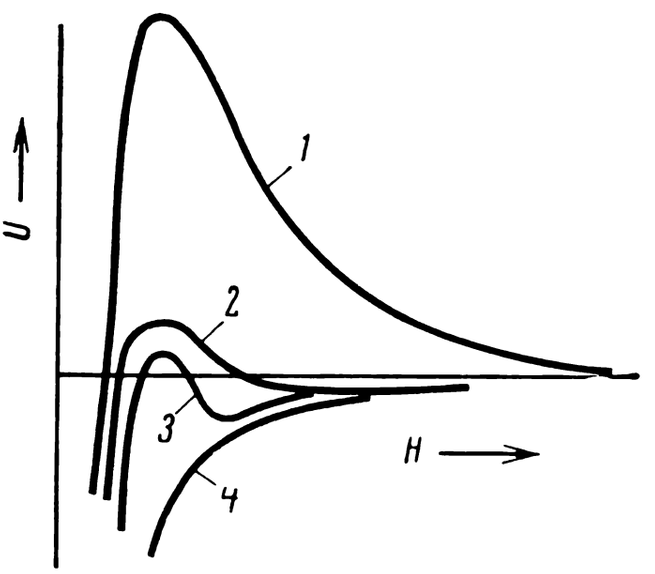

Fig. 9.13. Change in the shape of resultant curves, which characterize the interaction of two particles, as the electrolyte content increases.
The numeration of the curves grows as the φ_0-potential diminishes

particles of any shape does not increase infinitely. Instead, it tends to a finite limit and approaches it when the values of the surface potential are higher than 100 mV (Fig. 9.12). Because of this property, being a saturation of forces, as it were, we can speak of the force of interaction between maximally charged surfaces as a quantity which does not depend on the precise values of the surface potential.

This conclusion, though difficult to understand at first glance, is explained by the fact that the attraction of counterions to the particle surface increases with the φ_0-potential. Thus, as the charge of the inner "plate" of the electric double layer and the surface potential grow, the external field of the "plate "becomes more screened by counterions. Therefore, the intensity of the electric field at the periphery of ionic atmospheres and the forces of interaction between both particles no longer grow. Consequently, if colloidal particles are charged highly enough, their interaction depends only on the charge of the counterions which screen the action of the inner "plate" of the double layer and determine its thickness.

When an indifferent electrolyte is added to a system, the diffused part of the electric double layer is compressed and the thickness of the ionic atmospheres diminishes. At the same time, the compression of the ionic layer deepens the secondary potential minimum, thus making further aggregation more probable. Fig. 9.13 shows a change in the shape of the potential curves of the pairwise interaction between particles as the content of indifferent electrolytes in a system increases.

Deryagin and Landau calculated that the energy barrier, in the diagram for the energy of interaction as a function of the distance between colloidal particles, disappears at the coagulation threshold γ which is determined by the formula

$$\gamma = C \frac{\varepsilon^3 (kT)^5}{A^2 e^6 z^6} \tag{9.44}$$

where C = constant which depends little on electrolyte asymmetry, i.e., on the ratio between the number of charges of the cation and that of the anion;
e = electron charge;
z = counterion valency.

As expected, the threshold of concentration coagulation depends not on the φ_0-potential, but on the constant A, the dielectric constant ε of a solution, temperature T, and the counterion valency z. An ion bearing a charge of the same sign as that of a colloidal particle affects coagulation to a small extent, somewhat changing only the value of the coefficient C.

It also follows from Eq. (9.44) that the values of the coagulation threshold for mono-, di-, tri- and tetravalent ions should be related to one another as

$$1 : (1/2)^6 : (1/3)^6 : (1/4)^6 \text{ or as } 1 : 0.016 : 0.0013 : 0.00024$$

In some cases, this series in the first approximation accords with the empirical data, expressed in the rule of Schulze and Hardy, and seems to theoretically substantiate it.

The mean values of the coagulation thresholds (in mmol/l) of some sols, reported by Overbeek, are given below. As we may see, the ratios of the experimentally determined thresholds of coagulation by ions of different valencies (I, II, III, IV) coincide quite well with the theoretically calculated data (especially for coagulation by mono- and divalent ions).

The deviations observed can be attributed to the following circumstances.

First of all, experiments in determining the coagulation thresholds were carried out under different conditions, and minute factors which were often difficult to take into account distorted the results.

Sols Having Negatively Charged Particles

	Ionic valency			
	I	II	III	IV
Coagulation threshold γ of the As_2S_3 sol . .	55	0.69	0.091	0.09
Ratio	1	0.013	0.0017	0.0017
Coagulation threshold γ of the Au sol . .	24	0.38	0.006	0.0009
Ratio	1	0.016	0.0003	0.00004
Coagulation threshold γ of the AgI sol . .	142	2.43	0.068	0.013
Ratio	1	0.017	0.0005	0.0001

Sols Having Positively Charged Particles

	Ionic valency			
	I	II	III	IV
Coagulation threshold γ of the Fe_2O_3 sol . .	11.8	0.21	—	—
Ratio	1.0	0.018	—	—
Coagulation threshold γ of the Al_2O_3 sol . .	52	0.63	0.08	0.053
Ratio	1.0	0.012	0.0015	0.001

Moreover, even the same sols, used in experiments by various authors, possessed different characteristics, such as dispersity, which also affected the results.

Secondly, in determining the coagulation threshold, an electrolyte is usually taken in an amount required for coagulating a sol which is still not completely astabilized. But the ratio of the coagulation threshold values thus found to the concentration values corresponding to the coagulation of a completely astabilized sol remains unknown, and the ratio may be different for various electrolytes.

Thirdly, in coagulation, the actually found electrolyte concentration may considerably differ from the calculated one owing to ion exchange, especially when the coagulation threshold is low.

However, experimental data recently obtained show that the rule of Schulze and Hardy is inapplicable in some cases as the Deryagin-Landau law z^6. Considerably great deviations from such a regularity are often observed in experiments, i.e., the coagulating action of electrolytes in some cases is proportional to the counterion valency raised to a power less than the sixth. According to I. Yefremov and O. Usyarov, this deviation is due to the interaction between particles in the secondary potential hole, causing either the formation of flocculi of rather low strength or gelation.

The following conclusions can be drawn if we generalize everything what we have discussed above concerning neutralization and concentration coagulations.

When the potential φ_0 of particles is low, sol stability depends on the value of the surface potential, and adsorption phenomena determine the coagulation process; as we have seen, this explains the rule of Eilers and Korff. The coagulation of a sol having highly

charged particles is interpreted by the DLVO theory in terms of the compression of the electric double layer, as in the case of the rule of Schulze and Hardy. Both rules are applicable to sols of the same nature, and sometimes to sols of the same electrolytic composition.

7. EFFECT OF THE DIMENSIONS AND CONCENTRATION OF PARTICLES ON THEIR INTERACTION IN DISPERSED SYSTEMS

The DLVO theory is confined to a consideration of the potential curves for two disperse particles because coagulation in diluted sols is determined by the interaction between two particles which is the basis of Smoluchowski's and Fuchs' theories of coagulation kinetics. However, interactions between several particles must be taken into account in order to determine the conditions of the stability of concentrated sols. Such sols have not only sufficiently high stability, but also an ordered arrangement of particles similar to the points of a crystal lattice, for example, in some viruses and monodispersed latices. To have the ordered arrangement, a system must be sufficiently monodispersed. As J. Bernal and I. Fankuchen had noted, the ordered arrangement indicates the long-range forces between colloidal particles.

A method of plotting the curves for the interaction between three flat particles was worked out by Yefremov and Nerpin. It follows from the potential curves which they plotted that, at a low concentration of the dispersed phase, the potential holes become less deep and more blurred as particles grow thicker; and the potential barrier becomes steeper. At a high concentration of the dispersed phase, the potential holes are less deep for thin particles. Lastly, at equal and sufficiently great distances between thick and thin flat particles, the energy barrier is higher for thin particles, and this makes thin plates more stable. As a dispersed phase becomes more concentrated, the distance between surfaces and, consequently, stability sharply diminish for minute particles, causing their aggregation at concentrations when slightly dispersed systems can still be stable. Such aggregation is caused by "crowdedness", when the particles, even regardless of Brownian motion, turn out to be at distances when they are forced to slide down to the primary potential hole. In this case, aggregative stability is upset by a mechanism which differs from coagulation by electrolytes.

These conclusions were drawn after a consideration of a model system consisting of three flat particles; in this case, the charge (or potential) of the particle surface, and the electrolyte concentration must be constant. However, notwithstanding the simplifications allowed, these conclusions qualitatively conform also with the

experimental data obtained for systems consisting of many particles, i.e., when real dispersed systems were being investigated.

A similar method is used also for studying the effect of the concentration of the dispersed phase of lyophobic sols on their stability at different electrolyte concentrations. The considerably great differences in the coagulation of diluted lyophobic sols by electrolytes and the disturbance of the stability of concentrated lyophobic sols can be understood when account is taken of the interaction between several colloidal particles. In particular, the stability of concentrated systems must pass through a maximum as particles grow larger when the volume concentration of the dispersed phase is constant. This conclusion was experimentally confirmed by R. Ottewill and D. Shaw. If the numerical concentration of particles remains unchanged, the stability of a system diminishes monotonously as particles become larger. At the same time, large spherical particles and thick plate-like particles are characterized by the presence of a deep secondary minimum on the potential curves; as a result, the processes of long-range aggregation must be especially common in slightly dispersed systems.

8. IMPORTANCE OF ADSORPTION PHENOMENA TO COAGULATION

As we have already seen, colloidal systems can coagulate either by the neutralization mechanism or by the concentration mechanism. However, in most cases, coagulation occurs by both of these mechanisms simultaneously. The neutralization mechanism of the coagulation of lyosols is very important to real systems and depends on adsorption phenomena, as was indicated by many authors. Therefore, a quantitative account of the effect of adsorption on coagulation is necessary to further develop the theory of the stability and coagulation of systems stabilized with ions.

Let us briefly consider the role of adsorption phenomena in the coagulation of colloidal solutions. Extremely contradictory data on this are found in literature because, until recently, all the researchers determined ion adsorption indirectly, i.e., by a change in the concentration of an appropriate ion in a solution before and after coagulation. If account is taken of the comparatively low extent of ion adsorption by colloidal particles and the inadequate precision of the analytical methods used, it becomes clear why the results obtained in early investigations are contradictory. In this connection, Yu. Glazman and D. Strazhesko used the direct radiometric method to determine the adsorption of ions by the particles of lyophobic sols. This made it possible to correctly estimate even the smallest amounts of adsorbed ions.

Let us consider the work done in the Soviet Union. Experiments were conducted mainly with typical hydrosols having negatively charged particles. The coagulating ions used were $\overset{*}{Na}^+$, $\overset{*}{Rb}^+$, $\overset{*}{Ag}^+$, $\overset{*}{Ca}^{2+}$, $\overset{*}{Sr}^{2+}$, $\overset{*}{Y}^{3+}$, and $\overset{*}{La}^{3+}$. It was enough to wash the coagulates with a 0.1 M solution of KCl twice for desorbing almost all the adsorbed cations. This indicates that the ion exchange is involved in the adsorption of counterions in sol coagulation. Consequently, even if quasimolecular adsorption of electrolytes occurs in the systems under consideration, it should play a strictly subordinate role.

The results of the experiments in which the effect of an electrolyte excess on the sorption of counterions was studied have shown that the sorption of cations increases with the electrolyte concentration. Thus, when electrolytes are introduced in an amount transcending the coagulation threshold, the potential-determining ions, being always present in the intermicellar liquid, are adsorbed additionally. As a result, the density of the charge of the surface of a dispersed phase grows as well as its sorption capacity.

The concentration of the stabilizing electrolyte in the intermicellar solution affected the sorption of counterions differently. For instance, the removal of dissolved hydrogen sulphide from a mercury sulphide sol considerably reduced (by 6-8 times) the sorption of the ions $\overset{*}{Ca}^{2+}$ and $\overset{*}{Rb}^+$; at the same time, the stability of the sol in the presence of these ions diminished considerably. However, as it follows from experiments and from data in literature, the sorption capacity and stability of AgI sols depended little on the content of stabilizing ions in a system.

In the coagulation of the hydrosols of As_2S_3, Sb_2S_3, HgS, AgI, and MgO, counterions of different valencies were adsorbed equivalently. Thus, the concept of the equivalence of the sorption of coagulate ions, being argued until recently, was directly and unambiguously confirmed for typical hydrophobic sols. This fact shows also that the Gouy-Chapman theory of the diffused layer cannot account for the regularities observed in experiments. The equivalence of the sorption of counterions can be interpreted only in terms of the structure of the electric double layer in accordance with Stern's concepts.

According to radiometric investigations, the adsorption of the co-ions of an electrolyte that were used for effecting coagulation, i.e., ions bearing a charge of the same sign as that of a colloidal particle, is very small except when ions have strongly pronounced adsorbability (e.g., the anion I^- and the cation Cs^+).

Besides the adsorption of ions of electrolytes having low molecular weight, it is necessary to consider the adsorption of surfactants by colloidal particles. Such adsorption is of great interest because it

causes a change in all the properties of a colloidal system, particularly its resistance to electrolytes; therefore, it gives us a better understanding of the stability and coagulation of colloidal systems. In addition, the adsorption of surfactants by dispersed systems is also of great practical importance.

The stability and coagulation of the sols of ferric hydroxide and arsenic sulphide were studied in the presence of non-ionogenic surfactants to be adsorbed whose diphilic molecules consist of a non-polar hydrocarbon radical and a polar polyhydroxyethylene chain. The effect of non-ionogenic surfactants on colloidal systems differed even qualitatively, depending on the intensity of the interaction between the surface of colloidal particles and the dispersion medium. When concentrations of surfactants in a system were low, they did not make ferric hydroxide particles more hydrophilic and reduced the resistance of the hydrosol to electrolytes. This is apparently connected with the intermediate nature of the $Fe(OH)_3$ sol whose particles are sufficiently hydrophilic. At high concentrations, non-ionogenic surfactants caused the coagulation of the $Fe(OH)_3$ sol.

A completely different behaviour was observed for the hydrosol of arsenic sulphide in which the highly hydrophobic surface of colloidal particles became hydrophilic as a result of the oriented adsorption of molecules of non-ionogenic surfactants. At very low concentrations of these surfactants, when the degree of hydrophily was low, either the sensitivity to monovalent ions grew or resistance to di- and trivalent counterions increased quite inconsiderably. Sensitization by monovalent ions can be attributed to the interaction (attraction) between the adsorbed dipole molecules of surfactants. As the surface of a dispersed phase was occupied with adsorbed molecules of surfactants, the degree of the hydrophily of particles and the resistance of the As_2S_3 sol increased, and the lyophilized arsenic sulphide sol underwent coagulation only at high concentrations of an electrolyte having a low molecular weight.

The results obtained show that the surface of arsenic sulphide particles is modified as a result of the oriented adsorption of molecules of non-ionogenic surfactants. A typical hydrophobic colloidal solution of As_2S_3 turns into a sol having lyophilic properties whose aggregative stability is determined by the hydrated adsorption layers of a non-ionogenic stabilizer that are formed around particles of a dispersed phase. The oriented adsorption of molecules of non-ionogenic surfactants on the particle surface was ascertained experimentally.

The stability of the AgI and AgBr hydrosols was studied in the presence of polyethylene glycol and its alkyl ethers (non-ionogenic surfactants), and also sodium salts of various derivatives of sulphosuccinic acid and of butyl naphthalene disulphonic acid (ionogenic surfactants).

In this work, the same regularities as those concerning the above-mentioned action of surfactants on the properties of the As_2S_3 sol were generally observed, the difference being that alkyl ethers of polyethylene glycol caused a reversal of charge of the positive particles of the AgI sol. This phenomenon was attributed to the imposition of the adsorption jump of the potential, which originates in the layer of polar molecules of polyethylene glycol alkyl ethers oriented at the surface of the dispersed phase, on the potential of the electric double layer.

The degree of stabilization of sols was found to depend on their "age" and concentration. The AgI sol had the greatest stability on the attainment of a definite (apparently, almost maximum) density of the covering of colloidal particles with a monolayer of the adsorbed molecules of polyethylene glycol alkyl ethers.

The character of the coagulation of AgI sols containing non-ionogenic surfactants indicates that the high stability of systems in this case is mainly caused by the non-electrostatic forces although colloidal particles bear electric charges in the presence of a non-ionogenic stabilizer.

The effect of surfactants on the stability of AgBr sols has revealed that methyl ether of polyethylene glycol inconsiderably increases the stability of the colloidal solutions of silver bromide. Even when the ether content was relatively high, the values of the threshold of coagulation of sols by ions of different valencies greatly differed from one another. This means that AgBr sols remain ion-stabilized in the presence of methyl ether of polyethylene glycol that is poorly adsorbed by particles. But sol properties radically changed when the better adsorbable dodecyl ether of polyethylene glycol was added to the colloidal AgBr solutions. Sols became very stable, coagulated only at high concentrations of electrolytes, and the valency of counterions no longer affected their coagulating action. Thus, the stability of AgBr sols stabilized by this non-ionogenic surfactant is due to the non-ionic component of disjoining pressure. This component originates when the boundary layers of water having a special structure overlap; these layers hydrate the hydrophilic groups of surfactant molecules adsorbed on sol particles. The same stabilization mechanism is involved in other cases when similar substances are adsorbed on particles of hydrophobic sols.

AgBr hydrosols were stabilized by polyethylene glycols only when the hydroxyethylene chain contained more than a hundred units; this stabilization was the more pronounced, the higher was the molecular weight of a non-ionogenic surfactant. The character of coagulation of these systems indicates the formation of hydrophilic sols in such cases.

Hitherto, we discussed the adsorption of counterions by colloidal particles. But there are data to the effect that ions whose charge

is of the same sign as that of a colloidal particle can also be adsorbed if they have a sufficiently high adsorption potential (e.g., I^-). The hydration of ions plays a considerably great role in this case, and a diminution in hydration as a rule promotes their adsorption.

Such was the view held by S. Ghosh, N. Dhar, and others in the 1930's. Its correctness was recently confirmed by S. Teletov. In investigating the hydrosols of ferric hydroxide, he discovered that the differences in the coagulating power of metal acetates are caused by the action of the co-ions, i.e., ions whose charge is of the same sign as that of the $Fe(OH)_3$ particle. He used polarography, colorimetry, and radiometry to find that copper and zinc cations are adsorbed on the positively charged particles of metal hydroxides.

However, some researchers question the ability of ions whose charge is of the same sign as that of the dispersed phase to be adsorbed on it and thus increase the charge. For example, Pauli believes that ions whose charge is of the same sign as that of a particle reduce the activity of counterions in a solution as a result of which the ζ_{crit}-potential grows when an indifferent electrolyte is introduced. This ability to reduce the activity of counterions is the greater, the higher is the valency of the ions of an indifferent electrolyte that bear a charge of opposite sign. Another explanation for a growth in the ζ_{crit}-potential when an indifferent electrolyte is introduced was proposed by J. Bikerman and also by A. Rutgers. According to them, an increase in the ζ_{crit}-potential is apparent in this case because surface conductivity was usually not taken into account when the potential was being calculated. When the appropriate corrections were made, these authors did not observe a growth in the critical electrokinetic potential of colloidal particles as indifferent electrolytes were added to a system.

9. PARTICULAR PHENOMENA OBSERVED IN COAGULATION BY ELECTROLYTES

Among the particular phenomena observed in coagulation by electrolytes are the phenomenon of irregular series, the antagonism and synergism of ions in coagulation, the "accustoming" of sols to the action of electrolytes, and colloidal protection.

Phenomenon of irregular series. This phenomenon is observed when electrolytes which contain polyvalent ions bearing a charge whose sign is opposite to that of a particle are introduced into colloidal systems. Its essence is that when various, ever increasing amounts of electrolytes are added to aliquots of a sol, it at first remains stable, then coagulates within a definite concentration

range, afterwards becomes stable again, and finally, coagulation reoccurs for the last time when the electrolyte content is high. Such a phenomenon can be caused also by large organic ions of dyes or alkaloids.

The phenomenon of irregular series occurs because there are not enough polyvalent ions to coagulate a sol when the amount of an electrolyte introduced is very small. At this concentration of an electrolyte, the ζ-potential of particles is higher than its critical

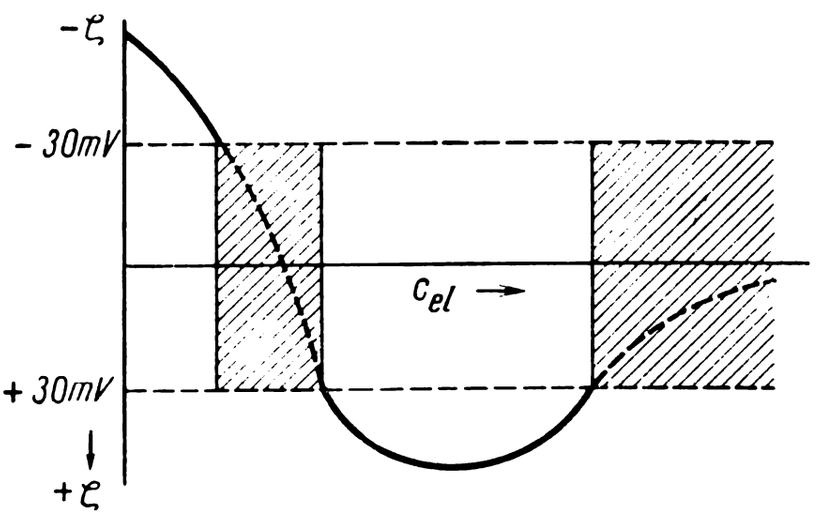

Fig. 9.14. Alternation of zones of stability and instability when an electrolyte having polyvalent cations is added to a sol with negatively charged particles. Zones of instability are crosshatched

value. The ions of an electrolyte exhibit coagulating action when its amount is greater. This concentration range corresponds to the values of the electrokinetic potential of particles between ζ_{crit} of one sign and ζ_{crit} of the opposite sign. At even higher concentrations, polyvalent ions reverse the charge of colloidal particles, and a sol becomes stable again. In this range, the ζ-potential is higher than the critical value, but it is opposite in sign to the ζ-potential of particles of the initial sol. Lastly, when the content of the electrolyte introduced is high, polyvalent ions coagulate a sol again for the last time by the mechanism of concentration coagulation.

For sols having negatively charged particles and for polyvalent cations, the above-mentioned dependence is illustrated by a diagram in Fig. 9.14.

A widespread opinion now is that the charge of negative particles is reversed not by electrolytes having polyvalent cations, but by the products of their hydrolysis containing positive ions of oxides or their hydrates. Proof of this is that particle's charge is not reversed at all in acid solutions. In a weakly alkaline medium, the sign of a charge is changed by a very low concentration of a polyvalent ion; at higher pH values the recharge becomes impossible again because the hydroxide ions formed under these conditions bear a negative charge.

Such a viewpoint on the reversal of charge and the phenomenon of irregular series is confirmed by the fact that a reversal of charge occurs also when an electrolyte having divalent ions is added, provided the solubility of the appropriate hydroxides is low enough. For instance, the negative particles of the AgI sol can become positively charged if nitrates of cadmium, zinc, or magnesium and a sufficient amount of NaOH are added to it. Such a reversal of charge does not occur if $Ba(OH)_2$ is added to the AgI sol because the solubility of barium hydroxide is rather high.

Of course, the phenomenon of irregular series can be observed also when potential-determining ions are added to a sol, for example, when $AgNO_3$ is added to a sol of silver halide having negatively charged particles.

The phenomenon of irregular series has long been known and has received its name at a time when the reversal of charge of sol particles was studied insufficiently. In fact, the alternation of the regions of the stability and instability of lyosols when polyvalent ions are added is quite natural, and therefore the term "irregular series" is conventional.

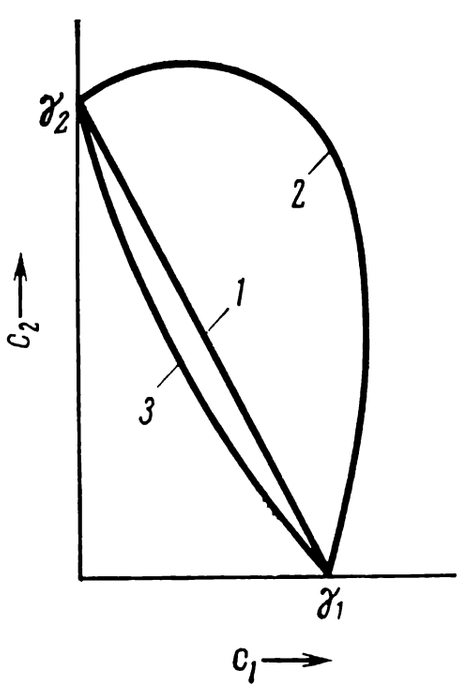

Fig. 9.15. Antagonism and synergism in the case of the coagulating action of electrolytes:

1—straight line characterizing the additive action of electrolytes; *2*—curve characterizing antagonism of electrolytes; *3*—curve characterizing synergism of electrolytes

Antagonism and synergism of electrolytes. The phenomena of the synergism and antagonism of electrolytes can be observed when sols are coagulated by mixtures of some electrolytes. These phenomena are of great practical importance because, even if one coagulating electrolyte is added to a colloidal system, coagulation occurs actually under the action of at least two electrolytes since a system contains a stabilizing electrolyte. In addition, mixtures of several (usually two) electrolytes are often used in technological processes for coagulation.

Three extreme cases can be observed in the coagulation of a sol by a mixture of two electrolytes.

1. The additive action of electrolytes. In Fig. 9.15, this case is characterized by the straight line *1* which connects the values of the thresholds of coagulation γ_1 and γ_2 by each electrolyte (the values of the concentration of one electrolyte are plotted on the abscissa,

and those of the other, on the ordinate). Electrolytes act independently, as it were, of one another.

2. Antagonism of electrolytes (curve *2*). The electrolytes counteract, as it were, one another and in order to coagulate a sol they should be added in an amount greater than that required by the additivity law.

3. Synergism of electrolytes (curve *3*). The electrolytes aid, as it were, one another and in order to coagulate a sol their amount should be less than that required by the additivity law.

Additivity is usually observed when the coagulating powers of both electrolytes are similar (i.e., when they contain counterions of the same valency). Antagonism occurs when there is a great difference in the coagulating power of electrolytes. It is difficult to formulate the conditions under which synergism is found.

Several theories have been proposed to explain the antagonistic action of electrolytes in coagulation.

Freundlich, the founder of the adsorption theory of coagulation, believed that the cause of antagonism was the ability of the ion of one electrolyte to reduce the adsorbability and, consequently, coagulating power of the ion of another electrolyte.

According to Odén, Ghosh, Dhar, and Kruyt, the antagonism of ions is found because, when an electrolytic mixture is introduced, the ions of one of the electrolytes adsorb on particles whose charge is of the same sign and increase their ζ-potential and, consequently, the stability of a system.

The first quantitative theory of coagulation by mixtures of electrolytes was evolved by Yu. Glazman basing on the modern physical theory of the coagulation of lyophobic sols. According to it, the antagonism of ions (and also the opposite effect, synergism) for highly charged sols is caused by electrostatic interactions in the diffuse atmospheres of colloidal particles, and for sols having a low charge, it may be caused by the competition of ions for sites in the adsorption layer.

In 1961, a more complicated theory of the coagulating action of an electrolytic mixture was proposed; it takes account of adsorption phenomena and makes it possible to find the critical concentrations of a mixture by the critical potentials and to determine the ability to adsorb individual components. According to the basic principles of this theory, account must be taken of the ratio between the electrostatic component and the van der Waals component of the energy (or force) of interaction between particles.

In several cases, the coagulating action of a mixture of electrolytes can be affected by the chemical reaction between their ions, yielding complexes or insoluble compounds that do not produce a coagulating effect. An example is the coagulation of the AgI sol by a mixture

of the electrolytes K_2SO_4 and $Th(NO_3)_4$ that form the complex $K_2[Th(SO_4)_3]$ which has no coagulating power.

Accustoming of colloidal systems. Colloidal systems sometimes lose stability as a larger amount of the coagulating electrolyte is introduced gradually than when it is added at once. The colloidal system becomes "accustomed", as it were, to an electrolyte, and hence the name of the phenomenon. There are also phenomena of negative accustoming, i.e., when an electrolyte is added slowly to a sol, its amount needed for coagulation is less than that when it is rapidly introduced.

There are several explanations for the positive and negative accustoming of colloidal systems.

According to the earliest theory, positive accustoming is due to the adsorption of an electrolyte by the gradually precipitating aggregated colloidal particles; as a result, its effective concentration in the intermicellar liquid diminishes and the amount of the coagulating electrolyte needed for completely coagulating a system is greater than that when it is introduced at once.

Ghosh and Dhar believe that positive accustoming occurs when colloidal particles slowly adsorb ions which bear a charge of the same sign as that of the particles; this somewhat increases the charge and makes a sol more stable. But ions whose charge is of the same sign as that of the colloidal particles are adsorbed rarely in coagulation, and therefore the theory of Ghosh and Dhar does not seem plausible.

V. Krestinskaya believes that positive accustoming and negative accustoming result from chemical changes in a colloidal system when electrolytes are added. For example, on an addition of HCl to the $Fe(OH)_3$ sol, positive accustoming occurs because, when the coagulating electrolyte is added rapidly, the sol coagulates just as under the action of an indifferent electrolyte. But when the coagulating electrolyte is added slowly, HCl reacts with the dispersed phase of the sol:

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

Thus, the amount of the dispersed phase decreases and that of the soluble iron salt, being a stabilizer, simultaneously increases, as a result of which the sol becomes more stable.

According to Krestinskaya, negative accustoming consists in the opposite phenomena: a decrease in the content of a stabilizer ($FeCl_3$) and an increase in the amount of the dispersed phase [$Fe(OH)_3$]. The negative accustoming of the ferric hydroxide sol can be caused, for instance, by adding alkalis which reduce the amount of $FeCl_3$ and increase the amount of $Fe(OH)_3$ in the sol.

The most substantiated viewpoint on the accustoming phenomenon is that based on the physical theory of stability. The height of the energy barrier which hinders the approach of sol particles slowly diminishes as the concentration of the electrolyte being added to a sol gradually grows. Accordingly, the number of the effective encounters of particles increases, causing aggregation. The coagulation threshold is usually broad in experiments, being in conformity with these concepts. As a result, when secondary phenomena are absent, negative rather than positive accustoming should generally occur. In other words, the cause of negative accustoming is that when an electrolyte is added slowly, its first aliquots act on a sol longer than when it is added at once. Each subsequent aliquot of an electrolyte acts on a changed, somewhat astabilized sol, and therefore the amount of an electrolyte required for coagulation is less.

It was also shown that the cases of positive accustoming described in literature are in fact the result of experimental errors. When an experiment is carried out accurately enough, negative accustoming is always observed, and this is in accord with theory. Positive accustoming occurs rarely when an electrolyte at very low concentrations peptizes a colloidal system.

Protection of colloidal particles and sensitization. Typical colloidal systems are very sensitive to the action of electrolytes. However, the stability of a system can be increased considerably when some substances of a high molecular weight are introduced into a sol and the adsorption layer is formed on the particle surface. Such a phenomenon has become known as colloidal protection.

Substances capable of engendering colloidal protection are proteins, carbohydrates, and pectins; for systems having a non-aqueous dispersion medium, such a substance is rubber. These substances are often called protective colloids although such a name is in essence incorrect and is applied only out of historic tradition.

A protective substance imparts, as it were, the properties of its solution to a sol. Sols which cannot be concentrated to a high content of a dispersed phase can be evaporated to dryness in the presence of protective substances having a high molecular weight, and then the dry residue can be converted to a colloid again. The electrophoretic mobility of the particles of sols that have adsorbed a sufficiently large amount of a protective substance is usually equal to the electrophoretic mobility of polymer molecules. Protected sols do not obey the rule of Schulze and Hardy when electrolytes are added, but behave like solutions of a protective substance having a high molecular weight; in order to precipitate a dispersed phase, the amount of the electrolyte needed is the same as that for precipitating a substance of high molecular weight. The reagent capable of precipitating a protective substance also precipitates the protec-

ted sol even when the initial sol is indifferent to the reagent. For instance, sols protected by gelatin lose stability on an addition of tannides which form an insoluble compound with gelatin; unprotected sols are insensitive to the action of tannides.

Zsigmondy proposed the "gold number" to characterize the protective action of substances having high molecular weight. This characteristic is the number of milligrams of a substance having high molecular weight which must be added to 10 ml of a red gold sol so as to prevent it from turning blue when 1 ml of a 10 per cent solution of sodium chloride is introduced into a system. Of course, the gold numbers thus obtained are conventional to a considerable extent because the protective action of a substance is affected by several factors: sol dispersity, the molecular weight of a protective substance, the pH of a system at which a test is being carried out, and so forth.

Sometimes, in determining the protective action of a substance having high molecular weight, the colloidal solutions of silver, congorubin, iron oxide, and others are used instead of the gold sol. In such cases, we speak of the silver, rubin, iron oxide, and other numbers, accordingly. Table 9.2 gives the values of these numbers for several protective substances.

Table 9.2. **Protective Action of Substances Having High Molecular Weight on Various Sols**

Protective substance	Number					
	gold	silver	rubin	iron oxide	sulphur	Prussian blue
Gelatin	0.01	0.035	2.5	5	0.00012	0.05
Hemoglobin	0.03-0.07	—	0.8	—	—	—
Gum arabic	0.5	1.25	—	25	0.024	5
Dextrin	20	100	—	20	0.125	250
Sodium caseinate	0.01	—	0.4	—	—	—
Potato starch	20	—	~ 20	—	—	—
Saponin	115	35	—	115	0.015	2.5
Egg albumin	2.5	1.5	2.0	15	0.025	25

As we have already seen, the mechanism of the protective action consists in the formation of an adsorption shell made out of a substance having high molecular weight around a colloidal particle. Electron micrographs proved the presence of such protective shells. For example, adsorption layers of methyl cellulose on polystyrene particles are 70-100 Å thick. If the protective layer is made out of macromolecules having polar or ionogenic groups, it can ensure

the induced solvation of a particle and a sufficiently high ζ-potential, and this makes a system more stable. In addition, according to the latest concepts, colloidal particles can become stabilized owing to the thermal motion and mutual repulsion of flexible macromolecules which are bound only partially with sol particles as a result of the adsorption of some of their parts (the entropy factor of stability).

The protection of colloidal particles is used in preparing medicines. It is often necessary to introduce a drug in a finely dispersed, colloidal state so that it would be uniformly distributed in the organism, dissolve, and produce the necessary effect. Protected sols or suspensions of drugs are just what meet this end. An example of such a preparation is highly dispersed silver stabilized with protein and known as collargol.

The addition of very small amounts of a substance having high molecular weight into a colloidal system sometimes causes sensitization rather than protection, i.e., the threshold of coagulation of a sol into which this substance is introduced turns out to be less than that of the initial sol.

If the macromolecules added into a system bear a charge opposite in sign to that of colloidal particles, sensitization is said to be a form of mutual coagulation whose mechanism will be considered below. But sensitization is observed also when sol particles and polymer molecules bear charges of the same sign. Such sensitization occurs because different parts of the same macromolecule are adsorbed on the surface of various colloidal particles and thus "paste together" particles into agglomerates. In this case, adsorption occurs usually after the addition of a coagulating electrolyte which promotes the adsorption of a substance having high molecular weight.

10. COAGULATION OF SOLS HAVING A NON-AQUEOUS MEDIUM BY ELECTROLYTES

Hitherto, we considered the coagulation of hydrosols by electrolytes. But sols having a non-aqueous medium can also be coagulated by electrolytes. The mechanism and characteristics of this coagulation have been studied to a far smaller extent.

Some authors have found that organosols having sufficiently high dielectric constant of the medium exhibit electrophoresis, and that there is a certain correlation between the electrophoretic mobility of particles and the stability of these systems. It follows that colloidal particles may have an electric double layer and the ζ-potential in organosols, like in hydrosols. The regularities obeyed by hydrosols are also valid for organosols in many cases: the rule of Schulze and Hardy is applicable to organosols, the phenomena of additivity

and antagonism are observed when they coagulate under the action of ions, and so forth. Thus, there is every reason to believe that the physical theory of coagulation can be applied, after making certain corrections in it, to sols having a non-aqueous dispersion medium.

Of course, the charge of organosol particles is usually not high owing to the lower dielectric constant of the medium and, consequently, the smaller dissociation of the molecules of a stabilizing electrolyte. However, since the electric double layer on organosol particles has a small capacity, the layer is highly diffused and very thick; as a result, even small charges are enough for the electrostatic forces of repulsion to originate. In general, organosols are far less stable than hydrosols.

The presence of an electric double layer on colloidal particles is far from always a cause of organosol stability. This stability can be due to solvation of particles as a result of the physical or chemical interaction between the medium and the dispersed phase.

The stability of colloidal systems in non-aqueous media is closely connected with the loss of the stability of hydrosols when some non-electrolytes are added to them. Hydrosols can be coagulated by such substances as ethanol, acetone, and monosaccharides in high concentrations. Non-electrolytes have a coagulating effect because they either reduce the dissociation of molecules contained in a system of stabilizing electrolytes or desolvate colloidal particles, thus ultimately bringing about sol coagulation.

11. HETEROCOAGULATION AND HETEROADAGULATION OF COLLOIDAL SYSTEMS

Besides coagulation or flocculation when similar particles coagulate into large aggregates (homocoagulation), heterogeneous particles often stick together (heterocoagulation), or particles of a dispersed system adhere to the extraneous surface introduced into this system (heteroadagulation).

The mutual coagulation or heterocoagulation of colloids, observed by H. Picton and S. Linder as early as 1897, was attributed to the action of the opposite charges on particles of the dispersed phase in both sols as a result of which particles coagulated. It was believed that, for complete coagulation, sols had to be taken in a quantitative ratio that would more or less completely neutralize the particle charge. However, it has been shown later that the mutual coagulation of colloidal systems can be observed also when the particles of both sols bear a charge of the same sign.

Heteroadagulation is observed, for instance, when colloidal particles, or particles which are more coarsely dispersed, are deposited on a fibre. It is used in tanning and dyeing, in pasting a paper

mass when paper is being produced, in the production of water-repellent textiles, and so forth.

According to Sokolov, Voyutsky, and Peskov, dispersed systems lose their stability in the presence of an extraneous surface because the surface adsorbs the stabilizer and, consequently, the content of the stabilizer in a sol diminishes.

Recently, Deryagin proposed a general theory of the interaction and adhesion of heterogeneous particles that is based on the same principles as those which he used in his consideration of homocoagulation. The theory makes it possible to explain coagulation when two sols interact or when an extraneous surface is introduced into a colloidal system.

Deryagin's theory of heterocoagulation is confirmed by experimental facts, particularly those obtained by Yu. Chernoberezhsky. It explains the phenomenon of "group coagulation" when aggregates containing identical particles are formed in mixtures of some colloidal systems and suspensions.

12. COAGULATION UNDER THE ACTION OF PHYSICAL FACTORS

Coagulation under the action of electrolytes is the most typical case of coagulation and is usually employed in technological processes when a colloidal system must be destroyed. But coagulation is often caused also by other, purely physical factors: the mechanical action on a colloidal system, the heating or the freezing of a sol, dilution or concentration, the action of visible and ultraviolet light, X-rays, radioactive radiation, an electric discharge, and ultrasound. A colloidal system can be destroyed spontaneously when it is stored away for a long time. The specific features and mechanism of non-electrolytic coagulation have not been studied well enough though such investigations could be very useful for comprehending coagulation in all its aspects and for gaining a correct understanding of its essence.

Let us briefly consider the data available on sol coagulation which occurs under the action of the most important physical factors.

Spontaneous coagulation. When colloidal systems are stored away, spontaneous coagulation can occur owing to slow chemical reactions in a sol or to the fact that some collisions between particles are effective and ultimately destroy a system.

The spontaneous diminution in the stability of a sol greatly depends on the conditions under which it is stored. For example, the stability of a mercury sulphide sol diminishes rather rapidly when it is kept in an open vessel because hydrogen sulphide, a stabi-

lizer of this freshly prepared sol, volatilizes from the solution. When a mercury sulphide sol is kept in an airtight vessel filled to the top, the sol not only does not coagulate, but becomes even more stable to the action of electrolytes because, under such conditions, instead of micelles of the type

$$\{m\,[HgS]\,nSH^- \cdot (n-x)\,H^+\}\,xH^+$$

more stable micelles of the type

$$\{m\,[HgS]\,nHgS_2^{2-} \cdot 2\,(n-x)\,H^+\}\,2xH^+$$

are gradually formed in a sol as a result of the chemisorption interaction between hydrogen sulphide and mercury sulphide.

Coagulation as a result of mechanical action. Such coagulation is observed when colloidal systems are being intensively stirred, when they are being pumped through pipes, and so forth. Coagulation by mechanical action occurs probably because the adsorption balance of a stabilizer at the surface of colloidal particles is temporarily upset. Such astabilized particles are thus able to approach one another to a distance at which molecular forces are effective and, consequently, stick together. Proof of such a mechanism of coagulation is the fact that a coagulate obtained as a result of mechanical coagulation always contains a smaller amount of a stabilizer than that obtained upon coagulation by electrolytes.

The systems which are more stable to mechanical action are usually more stable also to the action of electrolytes. The mechanical stability of colloidal systems was found to be connected with their stability on aging. The connection between all these factors is quite clear because mechanical stability, on the one hand, and the stability of a lyosol to electrolytes and on storage, on the other, are determined by the same factor: the properties of the electric double layer.

Colloidal systems may coagulate also as a result of vibratory effects and the action of the ultrasound. Vibratory coagulation is used in technological processes when pastes, concrete, and other systems are being produced. For example, the vibratory treatment of a concrete mixture at first destroys a coagulation structure in it, and the mixture consequently becomes more fluid, making it easier to fill the moulds with it. But a strong crystallization structure is formed on further vibratory treatment.

The coagulation of colloidal systems in the ultrasound field was observed as early as 1908. It was later ascertained that, in the precavitation region, exposure to ultrasound promotes coagulation, but its dispersion effect begins to prevail as the field intensity increases. In ultrasound fields of low intensity, small particles follow the medium while large ones, being very inert, are not entrained by

a liquid. Thus, small particles "pierce through" a medium and undergo the action of the molecular forces of large particles, which results in coagulation. D. Lychnikov and G. Martynov have found that the energy barrier can be overcome and coagulation can occur only when the amplitude of oscillation of particles is commensurable with the distance between them. The ultrasound field "throws over", as it were, minute particles from the secondary potential minimum to the primary one. If the particles are at great distances away from one another, the stability is not disturbed and a sol remains stable.

It was shown recently that the precipitates of the suspensions exposed to ultrasound contain particle chains which in all probability originate as a result of the polarization interaction between particles. It follows that the deformation of the electric double layer is important in the origination of structures in dispersed systems under the action of the ultrasound field.

Coagulation under the action of the electric field. It was discovered quite a long time ago that structures may be destroyed and

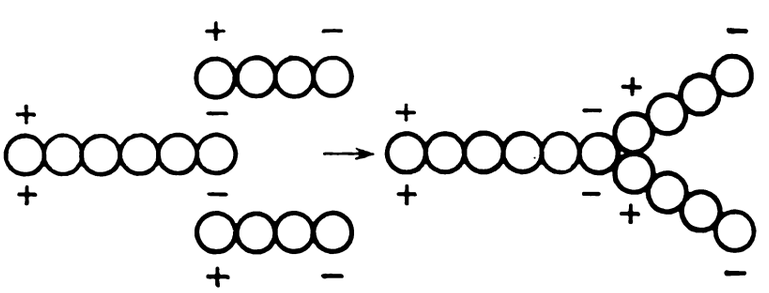

Fig. 9.16. Diagram of the interaction of dipole particles and the formation of chain aggregates

particle chains may be formed in sols and suspensions under the action of the alternating electric field. The action of the electric field on emulsions is especially important because it is used for dehydrating oil emulsions and treatment of water which contains impurities of mineral oils.

O. Usyarov, I. Lavrov, and I. Yefremov studied the effect of alternating and direct electric fields on the interaction between particles of synthetic rubbers dispersed in aliphatic alcohols and hexane. As they found, attraction originates in the polar media between particles in the electric field, especially at distances which are 2-3 times greater than the particle dimensions. As a result, linear aggregates, or chains, are formed; this is not observed in the case of non-polar hexane. Therefore, non-equilibrium electrosurface forces, caused by the deformation and polarization of the electric double layer, are responsible for the process of oriented aggregation. Secondary dendrite-like structures appear when chains interact with one another according to the diagram presented in Fig. 9.16. The removal of the electric field, when particles are fixed in a poten-

tial hole of little depth, causes the disintegration of aggregates or structures; such a phenomenon does not occur when particles are fixed in a deep potential hole.

Lavrov showed later that the application of the external alternating field of rather low intensity to aqueous suspensions of polyacrylonitrile causes particles to aggregate, orienting along the lines of force.

Coagulation when a colloidal system is diluted or concentrated. Coagulation which occasionally occurs when hydrosols are diluted with water can be attributed to the desorption of a stabilizing electrolyte from the particle surface to the dispersion medium, causing a diminution in the particle charge. In this case, the stabilizer may also be hydrolyzed, as a result of which a sol may lose its stability. In practice, when a colloidal system is being diluted with process water which contains electrolytes, coagulation may occur under the action of electrolytes.

It is far more difficult to explain coagulation when colloidal systems are being concentrated. Of course, when a colloidal system is being concentrated by evaporation, the concentration of electrolytes, which are always found in hydrosols, increases in it, and this may astabilize the system. However, hydrosols coagulate also when a system is being concentrated by ultrafiltration, i.e., when the composition of the dispersion medium does not change.

Some workers attribute sol coagulation in the course of concentration to a greater number of collisions between particles. But this explanation accords poorly with the fact that sols can coagulate spontaneously only when their concentration is higher than a critical value. The instability of a colloidal system above a definite concentration can presumably be attributed to an increase per unit volume in the content of not only an extraneous electrolyte, but also colloidal particles, which should be regarded as polyvalent ions, and likewise in the content of the corresponding counterions. Such an allowance is quite probable. Indeed, as Duclaux has shown, colloidal particles make their contribution to the electric conductivity of a system, and therefore there is every reason to believe that their charge should be taken into account when the ionic strength of a solution is being calculated.

Coagulation on heating or cooling. Heating even to the boiling point usually has a small effect on hydrosol stability. A diminution in aggregative stability on heating is occasionally observed apparently because the stabilizer is desorbed from the particle surface and Brownian motion intensifies. Both of these factors help to overcome the energy barrier when particles collide.

The cooling of hydrosols to a temperature which is higher than their freezing point usually has a little effect on hydrosol stability. Conversely, cooling accompanied by the freezing of a hydrosol often causes its coagulation which is as a rule the more complete, the lower is the temperature of cooling a sol and the longer a sol is kept in the frozen state.

According to A. Lottermoser, coagulation on freezing is affected not so much by temperature as by the extent to which a solution is converted into a crystal mass. He believes that microscopic crystals of water are formed between colloidal particles when it freezes. High pressure may develop in a frozen system owing to an increase in its volume. Particles of the dispersed phase are pressed together between crystals, deform, come into contact with one another, and agglomerate. Thus, a coagulate may be formed as a result of purely mechanical action which originates when a colloidal system is being frozen.

A. Dumansky took a different stand. According to him, crystals of pure water are gradually formed when a sol is being frozen; therefore, both the sol and the electrolytes contained in it are concentrated in the remaining unfrozen part of the system. Consequently, electrolyte concentration becomes so high that coagulation occurs. Dumansky supported his viewpoint by the observations made by Zsigmondy who found that a colloidal system on freezing was the more stable, the more resistant was it to the action of electrolytes or to dehydration.

Many properties of the coagulates of metal hydroxides change considerably as a result of their freezing and subsequent thawing: the precipitate volume and the moisture content diminish, whereas filterability improves. Such a change in the properties of coagulates is important to analytical chemistry, preparative radiochemistry, chemical technology, and to the purification of waters, including those which are radioactive.

10

STRUCTURAL-MECHANICAL PROPERTIES OF DISPERSED SYSTEMS

Having become acquainted with coagulation phenomena in the preceding chapter, we can now consider the structural-mechanical properties of dispersed systems. This could not be done earlier because structures in colloidal and microheterogeneous systems are formed as a result of their coagulation.

Colloidal and microheterogeneous systems with liquid and solid dispersion media, like all other condensed systems, have definite mechanical properties: viscosity, plasticity in many cases, elasticity, and strength. These properties are connected with the structure of such systems, and therefore they are often called *structural-mechanical* properties. They are also called *rheological* properties because the science of the flow of various bodies or, in a more general sense, the science of deformation processes which develop with time is known as *rheology*.

All colloidal and microheterogeneous dispersed systems, as we have already seen in Chap. 1, can be divided into freely dispersed and coherently dispersed ones. If the dispersion medium is a liquid, there may be also transitional systems whose particles are bound with one another into loose aggregates, but they do not form a continuous structure (cross-linked liquids). Apparently, such aggregates can be regarded as bits of a three-dimensional network which for some reason did not develop completely.

The concentration of a dispersed phase considerably affects the type of a system. In freely dispersed systems, the concentration of a dispersed phase cannot be very high; otherwise, particles will inevitably come into contact with one another. As a result, three-dimensional networks would be formed or, at least, the volume of a system would be filled up with particles of a dispersed phase to such an extent that it would be impossible for them to move freely relative to one another. Of course, when a stabilizer that prevents particles from drawing closer to one another and, consequently, hinders the action of molecular forces between them is introduced into a system, a considerable increase may be effected in the criti-

cal concentration at which bonds originate between elements of a structural network, i.e., in the concentration corresponding to a sufficiently high strength or structural viscosity of a system.

In coherently dispersed systems, the concentration of a dispersed phase can be very high. But the systems can be obtained also at very low concentrations of a dispersed phase, provided the particles are sufficiently anisodiametric, say, they are rods or plates. For instance, the sol of vanadium pentoxide with rod-like particles forms a gel containing 0.01-0.001 per cent of V_2O_5.

Of course, a structure of a colloidal system gives it definite rheological properties.

Since particles in freely dispersed systems are not bound with one another, the systems can undergo *viscous flow*, i.e., continuously change their shape with time under the action of even very low shearing stresses. In this case, the flow of these systems qualitatively obeys the same regularities as those obeyed by a pure dispersion medium. Quantitatively, the viscosity of such a system is usually higher than that of a pure medium.

Conversely, coherently dispersed systems possess, to a certain extent, the properties of solids owing to the forces of interaction between their particles, i.e., they are capable of retaining their shape, some strength, resilience, and often elasticity. However, as bonds between separate elements of the structure of a network are not firm, structures in coherently dispersed systems are destroyed readily and the systems acquire the ability to flow.

Cross-linked liquids are usually systems with a low concentration of a dispersed phase, but with a clearly defined tendency of particles to stick together.

Cross-linked liquids must apparently possess rheological properties which are intermediate ones between the properties of freely and coherently dispersed systems. These systems are able to flow, but, in this case, they do not obey the laws of flow of simple liquids which are not cross-linked.

The rheological properties of colloidal systems are strongly affected not only by the concentration of a dispersed phase in a system, but also by such factors as the nature of a dispersed phase, of the dispersion medium, and of the stabilizer. It is these factors that determine the effectiveness of molecular forces which operate between particles of a dispersed phase, on the one hand, and between particles and a solvent, on the other.

The nature of the structures formed in colloidal systems can be determined when the rheological properties of the systems are being studied. These properties are significant from the practical standpoint as well. Such systems as the soil, loams, cement grout, dyes-varnishes, and pastes are characterized by their structural-mechanical properties.

This chapter deals with the rheological properties of freely dispersed systems, coherently dispersed systems, and also systems of an intermediate type that have a liquid dispersion medium. The structural-mechanical properties of foams greatly differ from those of other systems having a liquid medium and are considered in Chap. 12; the mechanical properties of systems having a gaseous dispersion medium are treated in Chap. 11.

But before considering the rheological properties of systems having a liquid medium, it is necessary to become acquainted, even if briefly, with the arrangement and properties of structures which are formed in such systems.

1. ORIGINATION AND CHARACTERISTICS OF STRUCTURES IN COLLOIDAL SYSTEMS

According to A. Rabinerson and G. Fuchs, structures formed in highly dispersed systems can be classified by their density (number of bonds per unit volume). According to this classification, structures are divided into *friable* (*loose*) and *compact* ones. The first ones are characteristic of dispersed systems having anisodiametric particles, and the second ones often originate in systems having isodiametric particles. The former structures may convert into the latter ones when they age or are affected by coagulating factors.

Today, the widest use is made of the classification proposed by Rehbinder who divided structures in colloidal and microheterogeneous systems into *coagulation* (*thixotropically reversible*) and *condensation-crystallization* (*irreversibly destroying*) ones.

Coagulation structures. These are structures which usually originate as a result of a decrease in the aggregative stability of dispersed systems. In true coagulation, when particles completely lose stabilizing factors (the electric double layer, the solvate shell, etc.), they stick together to form compact aggregates. After attaining definite dimensions, these aggregates form dense coagulates (or coagulums). If a system is astabilized incompletely, only some regions of the particle surface lose, but incompletely, stabilizing factors; as a result, particles agglomerate in such regions and form a three-dimensional network whose cells contain the dispersion medium. As we say, *gelation** or *lyogel formation* occurs. The type of structure obtained by gelation is schematically illustrated in Fig. 10.1.

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* According to terminology used today, gelation is a term applied to the transition of a colloidal solution from a freely dispersed state (sol) to a coherently dispersed one (gel). The term "jellying" is used for a similar transition of a solution of a high molecular weight substance to a jelly.

When astabilization is sufficiently high, the interlayers of the dispersion medium between particles are completely forced out in places where they contact one another. As a result, particles come into direct contact with one another and the strongest, but at the same time the most brittle, coagulation structures are formed. However, sufficiently thick layers of the dispersion medium often remain in the place of particle-particle contact when astabilization is weaker. In other words, long-range action is observed between particles; its causes are considered in Chap. 9. The presence of a thin liquid interlayer between particles makes a structure less strong, but it gives the structure plasticity and, in some cases, elasticity. The thicker the interlayer of the medium between particles, the less is the effect of molecular forces which cause particles to adhere to one another, the weaker is a structure, and the more liquefied is a system.

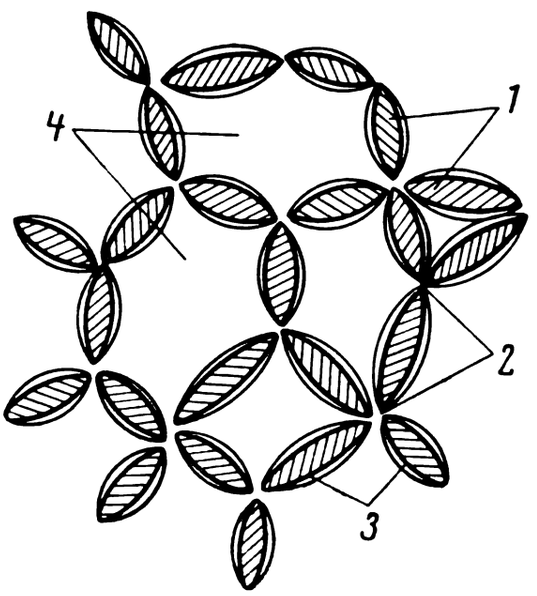

Fig. 10.1. Illustration of three-dimensional structures formed in a lyosol in the course of astabilization:
1—particles of the dispersed phase; *2*—surface regions of particles that have lost stability factor; *3*—surface regions that have retained stability factor; *4*—cells that are filled up with the dispersion medium

Several factors can affect gelation. The concentration of a dispersed phase affects the rate of gelation and gel strength because the number of contacts per unit volume of a system, and the rate of establishment of contacts grow with the numerical concentration.

A decrease in particle dimensions when the concentration of a dispersed phase is constant also promotes gelation. The shape of particles is important to gelation. Lyogel formation is facilitated if particles are anisodiametric and have ends, corners, and edges. In these places, electric double layers or solvate shells are developed to the least extent, and therefore that is where astabilized particles agglomerate. In addition, formation of the structure requires a far smaller amount of a dispersed phase which consists of rod-like or plate-like particles than that which consists of spherical particles.

Temperature also affects the rate of gelation and the properties of a gel. The duration of gelation decreases for the same reasons as that of coagulation when temperature increases. However, as temperature rises, lyophobic gels may be converted into cross-linked liquids owing to greater Brownian motion, and then they may become liquids which are not cross-linked as temperature rises further.

Mechanical action, such as stirring, usually hinders gelation. However, in some cases, the duration of gelation of aggregatively unstable sols having greatly anisodiametric particles (e.g., the V_2O_5 sol) can be reduced considerably if the vessel containing a sol is slowly revolved. This phenomenon, discovered by Freundlich, has become known as *rheopexy* (from Greek, meaning gelation in motion). Some researchers believe that rheopexy occurs because the parallel orientation of streaming elongated particles favours the establishment of contacts between them and, consequently, promotes gelation. Others hold that rheopexy is caused by slight turbulence which originates as a system moves and promotes the establishment of contact between particles.

A specific property of coagulation structures is *thixotropy* (from the Greek words "thixis" meaning to touch, and "tropia" meaning to turn, change), i.e., the ability of structures to change back with time after they have been destroyed by some mechanical action. In other words, thixotropy is the ability to undergo an isothermal reversible conversion of a sol into a gel. The bonds which were ruptured by mechanical action are restored as a result of accidental successful collisions of particles which are in Brownian motion. Such a gradual restoration of the structure and, consequently, the growth of its strength occur not only when a system is at rest, but also when a system flows at a rate less than that which determines a given degree of destruction of the original structure. When a transition is being made from one flow regime to another having a higher flow rate, additional destruction of the structure is often observed, though not always; this reduces the apparent viscosity and strength of a structure. Conversely, when a transition is being made from one flow regime to another having a lower rate, the structure is somewhat recovered and, consequently, the apparent viscosity and strength of a system grow.

Thixotropy is often encountered in nature. For example, it is exhibited by some soils (quicksand), by the protoplasm of living cells, and by myosin gels (this shows that the phenomenon plays a role in muscular work).

The ability of dispersed systems to exhibit thixotropy is used in engineering. For example, when oil wells are being drilled, clayey solutions are pumped through the well, i.e., it is washed in order to remove particles of ground drilled-out rock from it. The thixotropic properties of these solutions prevent both the sedimentation of rock particles in the well and the consequent drill jamming when drilling is stopped temporarily.

Another example of thixotropic systems used in practice is ordinary oil paints which are a suspension of mineral pigments in drying oil. Owing to the thixotropic properties of paints, they can be applied to vertical surfaces as a liquid after they have been mechanically

stirred; the paint does not run down because it is rapidly cross-linked. To make paints more thixotropic, special additives, such as polyamides and bentonites, are introduced into them. Rheological characteristics, including the thixotropy of such paints, and printing ink as well, were studied by A. Trapeznikov and his coworkers by methods which they worked out for determining ultimate strength and viscosity in a wide range of deformation rates. Thixotropy may be exhibited both in the destruction and formation of a continuous network (*strength thixotropy*) and in the destruction and restoration of particle aggregates (*viscous thixotropy*).

A phenomenon opposite of thixotropy is *dilatancy* which is exhibited in the small resistance of a system at low shearing stress and in high resistance at great shearing force. Dilatancy is characteristic of very concentrated, aggregatively stable suspensions which do not have constant contacts between particles. Reynolds who discovered this phenomenon in 1885 held that a system can move only when shearing stresses are low and the relative position of particles changes slightly. At high shearing stresses, particles come closer to one another and, accordingly, free space for flow diminishes; as a result, liquid motion is strongly hindered or even stops.

Tactoids and *Schiller's layers* are similar to thixotropic systems. Tactoids are dispersions having regions with well defined periodicity in the arrangement of anisodiametric particles which are parallel to one another. The anisotropic orientation of particles was discovered by taking the example of $Fe(OH)_3$ sols, several other inorganic and organic dispersions, and biocolloids, i.e., colonies of viruses and bacteria. Anisotropic regions are formed in such systems owing to equilibrium between the molecular forces of attraction and the electrostatic forces of repulsion that operate between particles which are usually dipoles.

Schiller's layers are colloidal precipitates made of lamellar particles arranged on horizontal planes which are several thousand angstroms away from one another. The characteristic structure of Schiller's layers is determined by the correlation between the forces of gravity and electrostatic repulsion of charged particles. Structures similar to Schiller's layers may originate under the action of other external fields, i.e., centrifugal, electric, and magnetic ones.

The fact that periodic structures are formed as a result of electrostatic repulsion when ionic atmospheres overlap is proven by a gradual decrease in distances between neighbouring particles as the electrolyte concentration grows. The quantitative theory of periodic colloidal structures was evolved by I. Efremov and S. Nerpin, and was specified in some respects by S. Dukhin and others. In this case, every particle is considered to be fixed in a potential hole formed by the cumulative action of its neighbours.

An analogue of periodic colloidal structures is the montmorillonite crystal swollen in aqueous solutions. In intracrystalline swelling, crystal planes which are about 10 Å thick draw apart and liquid interlayers are formed between them. A prerequisite of swelling is the saturation of a crystal by H^+, Li^+, or Na^+ ions. At very low concentrations, intracrystalline gap attains a width of 300 Å. When all the interlayers are the same, the periodic structure of a system is preserved and the thickness of interlayers can be measured by X-ray diffraction. The data obtained are in conformity with the DLVO theory. Such a swollen crystal is a good model of other periodic structures. As O. Usyarov has shown, the model can be used to detect the short-range and long-range potential holes, the energy barrier, and the effect of the ionic valency on the regularities of swelling.

If the concentration of a sufficiently monodispersed colloidal system which is protected from coagulation in the short-range potential hole by a high barrier becomes great, particles often form a quasicrystal lattice as they draw closer together, and they are arranged at equal distances from one another in it. When the dispersity of a system is high, particles undergo vibratory Brownian motion near their equilibrium positions.

Periodic colloidal structures are formed by many viruses, bacteria, monodispersed metal sols, vanadium pentoxide sols, and latices.

The formation of periodic structures means that the distance of each particle from the neighbouring ones corresponds to the long-range potential hole when a system borders on the free dispersion medium and, consequently, is not subjected to external pressure. In this case, distances between particles decrease when an electrolyte is added and increase when a system is diluted.

Periodic colloidal structures found more commonly are those which occupy the whole volume of a liquid medium and are confined on all sides by walls or by an interface with air. In this case, the potential hole, where every particle is retained, is formed as a result of summing the forces of repulsion by neighbouring particles. Therefore, the respective distances may be smaller than the abscissas of the long-range potential holes, and then the system, as we usually say, is in a "restrained" state. On further "compression" when the mean distances between neighbouring particles become smaller than the abscissas of potential barriers, equilibrium is upset and some particles agglomerate as they get into short-range potential holes while the remaining ones can retain their periodic arrangement.

But the periodic colloidal structure is usually in a state of only temporary equilibrium even before such "compression". Occasionally, one particle or another jumps from the position of equilibrium in a node of a quasicrystal lattice into a short-range potential hole. The defects of a quasicrystal lattice increase irreversibly and cannot

be "healed". Thus, unlike crystals, periodic colloidal structures are often not in a state of thermodynamic equilibrium, but are stable kinetically. In other words, their existence is determined by the slowness of the transition to an equilibrium state.

However, the possibility of the existence of equilibrium periodic structures cannot be ruled out in principle if a short-range minimum is absent. Several viruses, such as the tobacco mosaic virus, possibly belong to this category.

Efremov expounds the problem as it stands today and his own investigations of the periodic colloidal structures in a monograph*.

Systems having coagulation structures possess low strength, certain plasticity and elasticity. According to Rehbinder, the elastic properties of coagulation structures are engendered by a change in the entropy of a system as a result of the reorientation of structural elements constituting a system which accompanies a change in its form. Such structural elements are colloidal particles (unlike high molecular weight compounds where elastic deformation is connected with a change in the mutual orientation of units of molecular chains). Systems having coagulation structures exhibit also creep, i.e., the ability to slowly develop, in the course of flow, considerable residual deformation practically without a noticeable destruction of the three-dimensional network. The creep of a system is determined by high, though measurable, viscosity in the region of very low flow rates. The structure is considerably destroyed only at high flow rates in such systems because bonds between particles have no time to be restored and the destruction rate becomes higher than the restoration rate.

Syneresis is often found in systems having coagulation structures. It implies a spontaneous decrease in the dimensions of a gel with the simultaneous separation from it of the dispersion medium contained in its cells. Syneresis occurs because, in gelation, the small number of contacts that does not correspond to the maximum condensed state of a structure is formed between structural elements. The number of these contacts then increases as a result of the rearrangement of particles due to their thermal motion, and this causes a gel to be compressed and the dispersion medium to be pressed out of it. Syneresis is schematically illustrated in Fig. 10.2. As we may see, the number of rod-like particles forming a gel remains the same, but the number of their contact points sharply increases after syneresis.

Syneresis is favoured by all factors which promote coagulation, i.e., an increase in electrolyte concentration, an elevation of temperature, an introduction of desolvating agents into a system, and

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* I. F. Efremov, in *Surface and Colloid Science*, ed. E. Matijevic, Wiley Interscience, N.-Y., 1976, V. 8.

so forth. It is promoted also by the flexibility and mobility of elements of the coagulation structure. Therefore, syneresis is more pronounced in gels of high molecular weight substances made out of flexible macromolecules.

Systems having a coagulation structure from which the dispersion medium is removed by drying are capable of absorbing the medium when they come into contact with it. The absorption of the medium by a dry gel, or *xerogel* (from the Greek word "xeros", meaning dry),

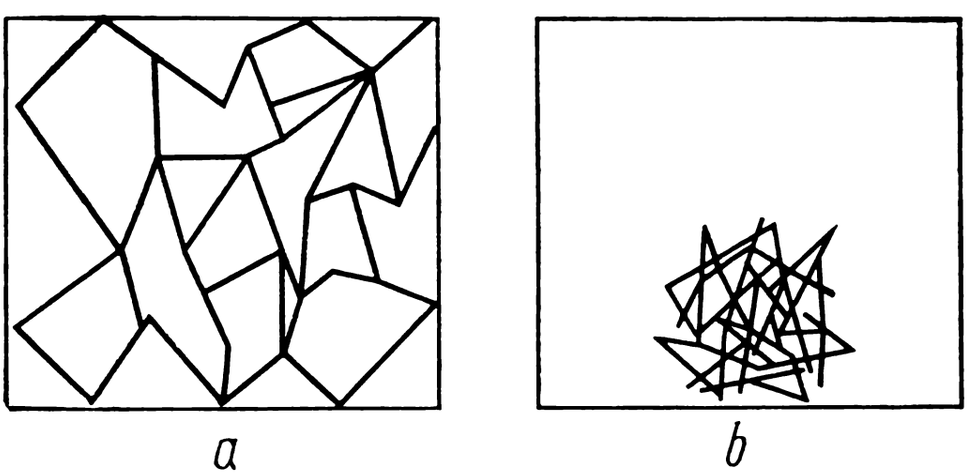

Fig. 10.2. Schematic illustration of syneresis:
a—system before syneresis; *b*—system after syneresis

may be caused either by simple capillary imbibition or by the drawing apart of the elements of the gel structure due to disjoining pressure and the filling up of the gaps with the medium. In the latter case, the xerogel is said to swell. It is evident that swelling is a process which is the opposite of syneresis. However, lyophobic xerogels swell to an inconsiderable extent because the places of contact are usually fixed rather firmly when a three-dimensional structure of lyophobic systems is being formed. Conversely, the gels of high molecular weight substances may swell to a great extent. The absorption of the medium by a dry gel or an ultimately strong coagulation structure causes plasticization, i.e., a sharp decrease in strength, but this is accompanied by an increased plasticity and elasticity of a given body.

Syneresis and swelling are considered in greater detail in Chap. 14.

Condensation-crystallization structures. These are structures whose particles are bound by chemical forces. The structures originate as a result of either the formation of strong chemical bonds between particles (condensation structures) or the intergrowth of crystals as a new phase is crystallized (crystallization structures).

Structures having such a nature of interparticle bonds cannot exhibit thixotropy, plasticity, and elasticity; they must, conversely, exhibit resilient-brittle properties. They are usually stronger than

coagulation structures. Systems having such structures cannot undergo syneresis or swell to a considerable extent.

The gel of silicic acid is a typical condensation structure. Crystallization structure formation is important to the solidification of mineral binders in building materials on the basis of cements, gypsum, or lime.

The presence in a system of surfactant modifying additives that change the shape and dimensions of crystals being formed, and also the conditions under which they intergrow, affect the formation of bonds and, consequently, the properties of these structures.

It is necessary to dwell, even briefly, on dispersed systems which have some properties in common with true cross-linked systems rather than a structure in the ordinary sense of the word. Such systems are, for example, highly concentrated, stabilized suspensions (pastes) and sediments.

In aggregatively stable suspensions whose particles are sufficiently solvated, almost the entire dispersion medium may be bound by solvation with a dispersed phase when the concentration of the phase is the highest (when particles are divided by a very thin liquid film). As a result, the viscosity of systems is very high.

The mechanical strength of such systems may sharply increase when surfactants are introduced into them; according to Deryagin, the molecules of surfactants are adsorbed and oriented on the particle surface, thus promoting the development and interaction of boundary solvate layers. The mechanical properties of a concentrated suspension can be enhanced also by introducing high molecular weight substances into it; these substances are adsorbed on the particle surface and cause the gelation of a liquid. In this case, gelation is promoted by particles of a dispersed phase which act as "active fillers".

The mechanical properties of concentrated systems whose particles of a dispersed phase have solvate shells are nevertheless lower than those of systems having coagulation structures and condensation-crystallization structures. In addition, owing to the formation of solvate shells on particles, a system is plasticized, its strength diminishes, and plastic-viscous properties appear in it whereas the resilient-brittle properties of a system are enhanced as three-dimensional structures originate.

Let us consider two possible cases of sedimentation of particles in sedimentatively unstable suspensions.

1. Aggregatively unstable suspensions sediment rapidly owing to the formation of aggregates; the sediment occupies a large volume because particles keep their random mutual arrangement which they acquire on contact. Such systems formed in sedimentation of suspensions are rather similar in their structure and properties to the coagulation structures which we considered above.

2. Aggregatively stable suspensions sediment slowly if the particles are sufficiently small; the particles which have settled to the bottom of a vessel remain separated from one another under the action of forces which hinder their aggregation. As a result, particles slip along one another and occupy a position which is characterized by the minimum potential energy and the greatest compactness of packing. The sediment thus obtained, if it is dense enough, may possess all the mechanical properties inherent in concentrated suspensions.

It follows that the volume of a sediment can characterize the degree of aggregative stability of a sedimenting suspension. This can be seen from the following example. If 40 g of quartz powder whose particle diameter is 1-5μm are mixed with 25 ml of water, an aggregatively stable suspension is formed; its stability is caused by the origination of hydrate shells or electric double layers around particles due to the ionization of silicic acid which is produced by interaction between SiO_2 and H_2O. In this suspension, only 8.5 mm of a sediment is formed after six hours, but it contains 54 per cent by volume of quartz.

An aggregatively unstable suspension is obtained if the same amount of quartz powder is distributed in the same volume of carbon tetrachloride which is incapable of forming solvate shells on particles and precludes the origination of an electric double layer. In this suspension, the layer of the sediment reaches a maximum thickness of 53 mm after merely 15 minutes of sedimentation, and it consists of only 7 per cent by volume of quartz.

Lastly, if 40 g of quartz powder are put into 25 ml of carbon tetrachloride into which a small amount of oleic acid has been introduced beforehand, a small quantity of a sediment of high density will be formed again as the suspension settles. This occurs because the molecules of oleic acid, while being adsorbed on quartz with their polar groups, impart hydrophobicity to the surface of particles, make them aggregatively stable in carbon tetrachloride, and thus promote the compact packing of particles in the sediment.

2. VISCOSITY OF TRUE AND COLLOIDAL SOLUTIONS

To have a better understanding of the specific features of viscosity of colloidal systems, it is necessary to recall the main concepts of viscosity and the mechanism of flow of simple low molecular weight liquids, such as water, ethanol and benzene. Suppose we used external force to put a thin liquid layer into motion, though not too fast, in a direction parallel to the plane of the liquid surface at a velocity of u_1, as is illustrated in Fig. 10.3. The underlying layers

will not remain at rest, but will also come into motion. The upper layer carries away the underlying layers owing to internal friction which originates between layers and is the outcome both of the chaotic thermal motion of molecules and intermolecular forces of attraction, the velocity of motion of these layers decreasing from the upper to the lower one because the lower layers retard the motion of the overlying ones. A decrease in this velocity is directly proportional to distance x from the upper layer to the lower one. Such

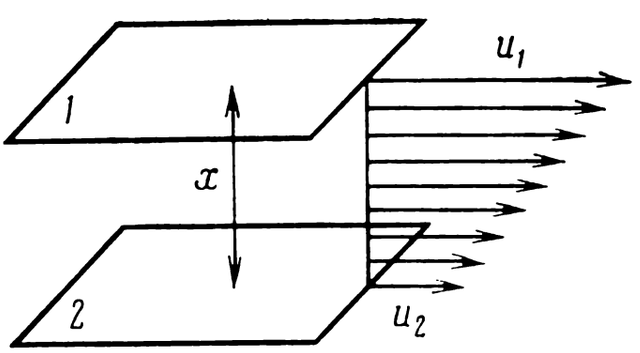

Fig. 10.3. Distribution of the velocities of motion of a liquid between two layers (*1* and *2*) which are moving parallel to one another and are at distance x

motion of liquid layers, known as *laminar flow*, can be caused by any small force, provided it acts for a sufficiently long time. Internal friction, like external one, is the cause of the dissipation of energy, i.e., its irreversible conversion into heat.

According to Newton's definition of viscosity, the internal friction force F which is equal in value but opposite in direction to the external force is proportional to the area s of layer to which this force is applied and to the gradient of the velocity of motion du/dx between layers:

$$F = \eta s\,(du/dx) \qquad (10.1)$$

where η is the proportionality factor known as the *viscosity coefficient* which depends on the nature of a liquid.

Relating force F to the shear area, Eq. (10.1) can be rewritten as

$$P = F/s = \eta\,(du/dx) \qquad (10.2)$$

where P is the shearing stress which maintains liquid flow.

It follows from Eq. (10.1) that the units of measurement of viscosity are g/(cm·sec).

The viscosity unit is called *poise* (P) in honour of the French scientist J. Poiseuille who first studied the motion of liquids in capillaries; a poise corresponds to the viscosity of a liquid at which a force of one dyne per square centimetre is needed to maintain a velocity gradient of one centimetre per second.

For comparatively low viscous liquids, the centipoise, a quantity which is a hundred times smaller, is used. The viscosity of water at 20 °C closely approximates one centipoise.

Viscosity of a liquid under the conditions of laminar flow, calculated by Newton's equation, depends neither on the technique of measurement nor on the type and dimensions of the viscometer used, i.e., it is an invariant characteristic of a given liquid.

The quantity $1/\eta$, a reciprocal of viscosity, is known as *fluidity*. It characterizes the mobility of a liquid under the action of external effects.

The laminar flow of a liquid in tubes is described by Poiseuille's equation*

$$v = \pi r^4 p/(8\eta l) \tag{10.3}$$

where v = bulk efflux velocity;
r and l = radius and length of a tube;
p = difference in pressures at tube ends;
η = liquid viscosity.

This equation was found empirically by Poiseuille in 1842.

Newton's equation and, consequently, Poiseuille's equation are valid for laminar flow, i.e., if a liquid moves as layers which have different velocities and do not mix with one another. Such a regime is observed only at comparatively low flow velocities. At high velocities, the nature of flow changes from a laminar to a *turbulent* one which is characterized by the origination of vortices in a moving liquid. If Newton's and Poiseuille's equations are applied to turbulent flow, the viscosity coefficient loses its ordinary meaning because its value now depends not only on the nature of a liquid, but also on the velocity of liquid motion. Evidently, in this case, we may speak only of effective or apparent viscosity, meaning the nominal quantity calculated for a given flow velocity by Newton's or Poiseuille's equation.

O. Reynolds showed in 1883 that when a liquid flows in a tube having a smooth wall, laminar motion becomes turbulent motion, when the Reynolds number Re exceeds a certain value. The Reynolds number or criterion is a dimensionless ratio

$$\mathrm{Re} = ur\rho/\eta \tag{10.4}$$

where ρ is liquid density.

As we can see from Eq. (10.4), laminar motion becomes turbulent motion at lower velocities, the greater is both the tube radius and the density of a liquid, and the less is its viscosity. The presence

* The derivation of this equation by integrating Newton's equation is given in textbooks of physics; see also S. S. Voyutsky, *Kurs kolloidnoi khimii* (Course in Colloid Chemistry), Khimiya, Moscow, 1964, p. 342.

of suspended particles, especially of irregular shape, in a liquid promotes early turbulence when laminar flow becomes turbulent flow at lower Re values.

Newton's or Poiseuille's equation quantitatively describes liquid flow, but it says nothing about its essence. To understand the process of liquid flow, it is important to have an idea of its molecular mechanism.

The mechanism of liquid flow can be conceived correctly only on the basis of the modern concepts of liquid structure evolved by Ya. Frenkel and H. Eyring (see Chap. 3).

Molecules of any liquid are in continuous thermal motion, moving relative to one another by their consecutive displacement into

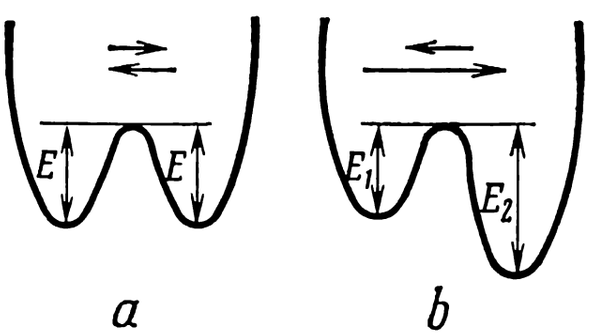

Fig. 10.4. Dependence of the potential energy of a molecule on its position near a hole:
a—when the external force field is absent; *b*—under the action of the external force field

holes which are in a liquid. As long as no external forces act on a liquid, displacement is equally probable in all directions. In this case, the dependence of the potential energy on the position of molecules near a hole can be described by Fig. 10.4*a*. But if a liquid is under the action of an external force field, which tends to displace molecules in a definite direction, the potential energy after a new level E_2 of molecules is attained will be less than that before their transition E_1. In this case, the potential hole is deformed and assumes the shape shown in Fig. 10.4*b*. Since jumps of molecules which cause a diminution of potential energy occur more frequently than those which cause an opposite phenomenon, chaotic motion acquires direction and the transfer of a substance, i.e., liquid flow, is observed.

The frequency of displacement of molecules in a liquid is the greater, the higher is kT, the average kinetic energy of thermal motion of a molecule, and it is the less, the more is the amount of work which must be done for a molecule to make a jump. It follows that, as temperature rises, the time taken for molecules to move to neighbouring equilibrium positions becomes less, and the liquid becomes more mobile at the same shearing stress. In addition, as temperature rises and the energy of thermal motion grows, an increasing number of molecules acquire energy needed for making a jump.

Lastly, as temperature rises, a liquid expands thermally, and then the number of holes and their dimensions increase. This causes a considerable decrease in internal friction or an increase in fluidity. For example, the viscosity of water changes by 2-3 per cent as temperature changes by 1 °C in a range of temperatures which are not too high.

As it follows from the molecular model of viscous flow, fluidity and viscosity change with temperature approximately according to the exponential law

$$1/\eta = A \exp(-E/kT) \tag{10.5}$$

or

$$\eta = A' \exp(E/kT) \tag{10.6}$$

where A and A' = coefficients which depend slightly on temperature;
E = activation energy which a molecule must acquire in order to jump to a new equilibrium position;
η = viscosity;
k = Boltzmann constant;
T = absolute temperature.

At certain values of fluidity or viscosity as a function of temperature, it is easy to find the value of activation energy by taking the logarithms of these equations because the relationship between $\ln \eta$ and $1/T$ must be expressed by a straight line. This graphic relationship for various liquids is a straight line only in a relatively narrow temperature range; when the range is wider, the line is usually not straight.

Experiments show that the activation energy of viscous flow of a liquid is equal to several kilocalories per mole.

DETERMINATION OF THE VISCOSITY OF LIQUIDS

The viscosity of liquids can be determined by various methods. Let us deal briefly only with the most important ones.

The falling-ball method. It consists in the determination of the velocity of the free fall of a ball having a known volume and mass in a liquid. To prevent the turbulent motion of a liquid, the velocity at which a ball falls should not be too high and the vessel in which it falls should be sufficiently wide. The viscosity coefficient is calculated by the equation which is easily derived from Eq. (3.39):

$$\eta = 2r^2 (\rho - \rho_0) g/(9u) \tag{10.7}$$

In determining viscosity by the velocity at which a ball falls, the experimenter solves a problem which is the opposite of the one

he has to solve for finding the radius of a suspension particle by the sedimentation rate.

It follows from Eq. (10.7) that the velocity at which a ball falls is inversely proportional to liquid viscosity. Such a relationship is observed also when a ball does not fall in a wide vessel, but moves in an inclined glass tube filled with a liquid, like in the Höppler viscometer.

The capillary method. The method is based on the measurement of the time it takes for a definite amount of a liquid to flow through a capillary whose radius and length are known. In this case, viscosity is calculated by the equation

$$\eta = \pi r^4 p\tau/(8lV) \qquad (10.8)$$

where V is the amount of a liquid that has flown out in time τ; the other symbols are the same as in Eq. (10.3).

Determination by rotary viscometers. The devices used for determining viscosity by this method consist of two coaxial cylinders. The test liquid is poured into an annular gap between them. One of the cylinders (usually the inner one) is brought into motion, for example, by a load, block, and a cord. After a very short period of time, a steady-state regime of liquid flow is established between cylinders. Viscosity is found by determining the number of revolutions of the rotating cylinder per unit time. Several designs of such a device have been elaborated by M. Volarovich in the Soviet Union.

Another variety of the rotary device, proposed by F. Shvedov as early as the last century, also consists of two coaxial cylinders; the outer one is brought into rotary motion at a constant speed by an electric motor, and the inner one is suspended on a thin elastic thread and has a meter showing the angle of rotation. Liquid is poured into the gap between cylinders. The outer cylinder on rotation carries away the liquid which causes the inner cylinder to rotate and twists it at some angle until the torque moment becomes equal to the friction moment. This angle is always proportional to viscosity because the thread suspending the inner cylinder is elastic.

The equation which connects rotational speed with the angle of rotation of the cylinder can be used to calculate viscosity when the constants of the device are known.

It is not the absolute, but the relative methods of determining viscosity that are used very often in practice, and this makes it possible to exclude the constants of devices from a calculation. In this case, the duration of the fall of a ball, the duration of efflux, or other parameters are recorded first for a standard liquid and then for the test liquid. Since the values of viscosity are proportional

to the measured quantities, the viscosity of a test liquid can be calculated by the results obtained when the viscosity of a standard liquid is known. As viscosity depends greatly on temperature, it should be measured always at a constant temperature, thermostating the device.

Methods of determining viscosity are considered at greater length in laboratory manuals of colloid chemistry.

Dependence of the effective viscosity of colloidal systems on the flow velocity. The flow of sols differs from that of simple individual liquids or true solutions of low molecular weight substances because colloidal particles whose dimensions considerably excel those of molecules are present in sols in a suspended state. Such particles change the paths of molecules of a flowing liquid and promote the mixing of layers. That is precisely why dispersed systems undergo early turbulence, i.e., laminar flow becomes turbulent flow at lower Reynolds numbers than those of liquids which do not contain suspended particles. In addition, colloidal particles narrow down the space occupied by a flowing liquid and thus increase the average velocity gradient in a direction which is perpendicular to liquid flow. As a result, the viscosity of a sol is always somewhat higher than that of a dispersion medium.

A characteristic of many sols is that they do not obey the relations expressed by Newton's and Poiseuille's equations. For simple liquids, the amount of liquid which passes through a capillary per unit time is directly proportional to the difference in pressure p at the capillary ends. Likewise, a direct dependence is observed for simple liquids between the angle of rotation of the inner cylinder and the speed of rotation of the outer one in a rotary device, such as Shvedov's viscometer. This dependence is absent for many sols, emulsions, and solutions of high molecular weight substances; viscosity calculated by the appropriate equation has a variable value and is a function of the velocity gradient. In other words, the viscosity of many dispersed systems is not an invariant characteristic of a system, but depends on the conditions under which it is determined, such as the velocity of liquid flow in a viscometer, and the type and dimensions of a device.

Newton's and Poiseuille's laws do not hold for colloidal systems having elongated and deformable particles, and also by cross-linked colloidal systems. The viscous flow of colloidal systems having elongated, rod-like particles is anomalous because, as shearing stress engendering flow increases, such particles become oriented by their long axis in the direction of flow, and then hydrodynamic resistance decreases and a liquid thus moves faster. Such an orientation of elongated particles can be easily proven by measuring sol birefringence at an ever growing gradient.

A similar dependence is observed for systems having particles which are being deformed, such as emulsions. Spherical drops of a dispersed phase become elongated ellipsoids as shearing stress and the flow velocity increase; this, of course, facilitates flow and reduces viscosity. The same phenomenon is also observed in the flow of solutions of high molecular weight compounds having flexible, coiled macromolecules. In this case, viscosity diminishes because molecules straighten out and orient themselves in the direction of flow. Of course, in all the foregoing cases, the matter in question is apparent or effective viscosity since the true viscosity of a liquid cannot depend on the flow velocity.

Cross-linked liquids also do not obey Newton's and Poiseuille's laws. It is expedient to consider the viscosity of such liquids separately owing to both its great practical importance and some fundamental features.

All liquids which obey Newton's law are known as *simple* ones; systems which are able to flow but do not obey Newton's equation are usually called *quasiviscous* ones. When working with a capillary viscometer, a very simple technique can be used to determine whether a test liquid is a simple or quasiviscous one. To this end, excess pressure p under the action of which a liquid flows is multiplied by the respective duration of the efflux of a definite amount of a liquid. Since Poiseuille's equation can be represented as

$$\eta = \frac{\pi r^4}{8lV} p\tau = kp\tau$$

it is quite clear that if the product $p\tau$ does not depend on pressure under which efflux occurs, a liquid is a simple one, and if it depends on this pressure, a liquid is a quasiviscous one. When using a rotary viscometer, such a criterion may also be the dependence or independence of the number of cylinder revolutions per unit time multiplied by the quantity of a load which allows the cylinder to revolve.

3. STRUCTURAL VISCOSITY

Cross-linked systems do not obey Newton's law because either bits of a structure that are not bound with one another are present in a liquid, or the continuous cross-linked network in it can be easily destroyed even when weak forces act on a system.

In the first case, a system in the event of flow behaves as a suspension of particles capable of being oriented or deformed. Bits of a cross-linked network are destroyed as a result of the different velocity at which layers flow, and, if they are elongated, orient themselves by their long axis in the direction of flow.

The second case is a more complicated one. At first Shvedov and then Bingham assumed that a system having a low-strength three-dimensional structure begins to flow only when shearing stress P excels a definite critical value θ which is necessary for destroying the structure, i.e., when $P - \theta > 0$. Bingham called such flow *plastic* flow, and critical (ultimate) shearing stress θ, the *yield point.*

Apparently, for systems having plastic flow, Newton's equation should be replaced by Bingham's equation

$$P - \theta = \eta' (du/dx)$$

or

$$P = \eta' (du/dx) + \theta \qquad (10.9)$$

where η' is viscosity which corresponds to the plastic flow of a system (*plastic viscosity*).

When there is no cross-linked network, the value of θ is apparently equal to zero, Bingham's equation becomes Newton's equation and plastic viscosity η' becomes true viscosity of a liquid. Bingham

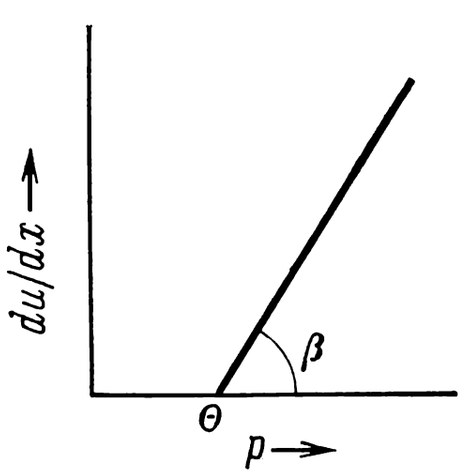

Fig. 10.5. Relationship between du/dx and P for a plastic system according to Bingham

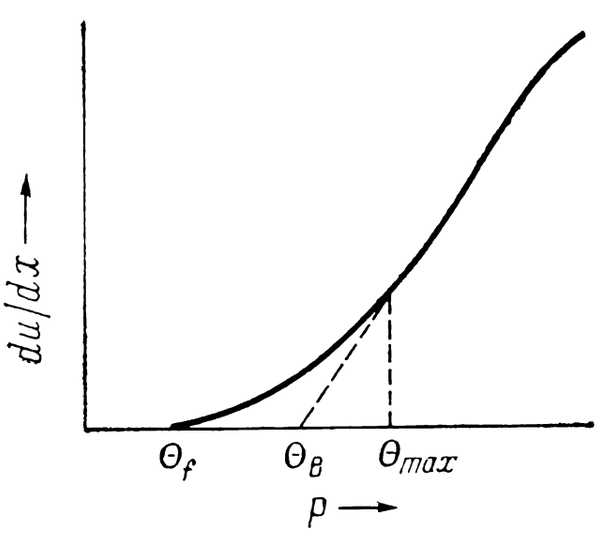

Fig. 10.6. Relationship between du/dx and P for a real plastic system

accepts that the viscosity of a system immediately becomes constant as soon as P excels θ and flow begins. Under such conditions, the dependence of du/dx on P is expressed by a straight line (see Fig. 10.5). According to this illustration, plastic viscosity can be expressed as

$$\eta' = \frac{P - \theta}{du/dx} = \cot \beta \qquad (10.10)$$

where β is the angle formed by the straight line and the abscissa.

An example of systems which obey Bingham's equation rather well is pastes made out of clay and grease. However, for most cross. inked colloidal systems, the dependence of du/dx on P is expressed not by a straight line, but by a curve (Fig. 10.6), because, as the

yield point is attained, the structure is destroyed not immediately, but gradually as a liquid gains momentum. Apparently, a distinction can be made between three critical shearing stresses: (1) θ_f—the first, or minimum, yield point which corresponds to the beginning of flow (the beginning of structural destruction;) (2) θ_B—the yield point according to Bingham which corresponds to a segment on the abscissa that is cut off by the continuation of the rectilinear segment of the curve; (3) θ_{max}—the maximum yield point which corresponds to the value of P when the curve becomes a straight line. Evidently, θ_{max} is the stress at which the structure in a liquid is completely destroyed. All the three yield points characterize the mechanical properties of a structure which exists in a system.

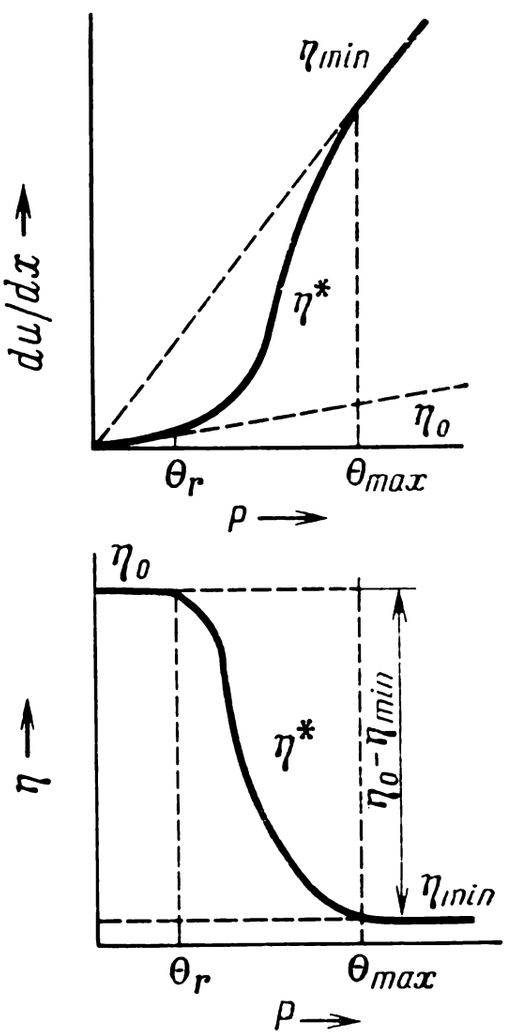

Fig. 10.7. Flow curves and the dependence of effective viscosity η^* on shearing stress P for cross-linked liquids (according to Rehbinder):

θ_r—shearing stress corresponding to the transition of creep to flow with measurable viscosity; θ_{max}—maximum yield point

In recent years, the structural viscosity of colloidal systems has been studied in detail by Rehbinder and his school, and also by Trapeznikov and his fellow workers. They have shown that two opposite processes, destruction and recovery, occur in a coagulation structure at any flow velocity. The state of equilibrium between these processes in steady-state flow is characterized by effective viscosity.

At low flow velocities, inconsiderable damage is done to a system since destruction which is connected with flow has time to be eliminated on the basis of thixotropy owing to the slowness of the flow process; the system flows almost without the decomposition of the structure, i.e., creep is observed.

At high flow rate, the structure of a system is destroyed to a considerable extent, and is recovered only slightly owing to the rapidity of the process.

For characterizing the flow of cross-linked liquids and plastic bodies, use should be made of not plastic, but effective viscosity η^* which diminishes with a growth in shearing stress in a system. At low

shearing stresses, effective viscosity has the highest value which is equal to η_0' of a liquid whose structure is almost intact. At high shearing stresses, effective viscosity diminishes to a minimum value η_{min}, i.e., to viscosity which corresponds to the complete destruction of a structure (provided laminar flow is maintained).

The flow curves (du/dx, P) and the dependence of viscosity on shearing stress for cross-linked systems, according to Rehbinder, are illustrated in Fig. 10.7.

The viscosity of cross-linked colloidal systems greatly depends on the conditions under which it is determined, particularly on the gradient of velocity at which it is measured. Therefore, the values of viscosity of such systems can be compared only when they are found in states which are characterized by the same values of the Reynolds number. For the same reasons, it is expedient to determine the viscosity of sols not at one value of shearing stress; instead, the curves of du/dx, P which characterize the rheological properties of a system in a sufficiently wide range of P values must be plotted. But even when measurements are taken under exactly the same conditions and the same viscometer is used, the values of viscosity found for the system may differ considerably, depending on its prehistory and on the time that has passed since the system was prepared. For example, when a colloidal system stands for a long time, its viscosity may gradually increase owing to the cross-linking process. Such a change in viscosity may be observed by taking the sols of ferric hydroxide or vanadium pentoxide as an example. On the other hand, as a result of mechanical action, e.g., when systems flow through a capillary, the structures formed in a system may be destroyed, and then its viscosity decreases. That is precisely why continuously diminishing values which tend to a definite limit are often obtained when viscosity measurements are taken successively by a capillary viscometer.

4. MECHANICAL PROPERTIES OF COLLOIDAL SYSTEMS EXHIBITING TRUE ELASTICITY

We regarded colloidal systems as liquids in the preceding section when we considered their structural-mechanical features. However, several properties of colloidal systems can be explained if they are regarded as solids. It is especially expedient to take the latter approach when studying colloidal systems which are resilient or elastic to a certain extent and are characterized by a true yield point (elastic limit), i.e., a shearing stress limit below which flow is hardly observed. Sufficiently concentrated solid-like gels and crystals having a condensation-crystallization structure as a rule possess such properties.

But before considering the mechanical properties of elastic gels, let us briefly deal with the shear modulus and stress relaxation time, the characteristics of systems which are important for understanding these properties.

Shear modulus E characterizes the rigidity of a body and its ability to retain its shape. This quantity can be calculated by Hooke's equation

$$\varepsilon = P/E \tag{10.11}$$

where ε = shearing strain in true solids;
P = shearing stress.

This equation is valid only at low strains because a body loses elastic properties and retains permanent strains at definite critical stress, known as the elastic limit. Shear modulus E depends on the nature of a body and temperature when the rate of load application is the same. For solids, the quantity E may attain very high values, but for true liquids, $E = 0$ because any arbitrarily small shearing stress causes liquid flow. The values of shear modulus E (in kgf/cm^2) for some substances are given below:

Gelatine	
0.5 per cent solution	4×10^{-10}
10 per cent solution (jelly)	5×10^{-2}
Raw rubber	1.7×10^{2}
Lead	4.8×10^{4}
Wood (oak)	8×10^{4}
Steel	8×10^{5}

Trapeznikov has shown that a characteristic rheological parameter of a system is ultimate reversible shearing strain ε_{max} which is attained in rapidly relaxing systems (for information on relaxation, see further) at a high strain rate. It may be diverse in different colloidal systems. For example, it usually constitutes several per cent or tens of per cent in pastes, but it may reach ten thousand per cent in elastic gels and some polymer solutions. Such values greatly excel the ordinary values of ultimate reversible shearing strains of raw rubbers.

Relaxation time is engendered because molecules or other structural elements of a system usually possess some mobility and can move relative to one another. As a result, stress created in a body owing to its deformation is capable of being "dissipated" to a considerable extent with time. Such a process of diminution of stress with time is known as *relaxation*; it is the outcome of thermal motion and has a quite general nature.

Several equations describing the strain of systems that are capable of relaxing have been proposed. The simplest one is Maxwell's equa-

tion which is derived from his theory of a viscoelastic body:

$$dP/d\tau = E\,(d\varepsilon/d\tau) - (P/\tau^*) \qquad (10.12)$$

where τ^* is the relaxation time constant.

Maxwell's equation gives qualitatively fundamental regularities of relaxation at constant temperature. If the strain of a body is kept constant ($\varepsilon = \text{const}$) then $d\varepsilon/d\tau = 0$, and it follows from the equation that stress P changes with time according to the law

$$(dP/d\tau) + (P/\tau^*) = 0 \qquad (10.13)$$

Integrating this equation, we obtain

$$P = P_0 e^{-\tau/\tau^*} \qquad (10.14)$$

Therefore, stress in a deformed body diminishes with time according to the exponential law, and the constant τ^* that characterizes the relaxation rate is equal to the length of time during which the initial stress of a body at constant strain diminishes by $e = 2.72$ times (e is the base of natural logarithms).

The relaxation time of liquids having low viscosity is very small owing to the great mobility of their molecules. As viscosity increases, the relaxation time of liquids grows and approximates that of the stress of solids. For crystals, the relaxation process occurs infinitely slowly. The time of relaxation of stress τ^* (in seconds) is given for some substances below:

Water	3×10^{-9}
Castor oil	2×10^{-2}
Copal varnish	2×10
Colophony (at 55 °C)	5×10
Gelatine, 0.5 per cent solution	8×10^{2}
Colophony (at 12 °C)	4×10^{6}
Ideal solids	∞

A very dilute 0.5 per cent aqueous gelatine solution has comparatively long relaxation time which is closer to that of the stress of solids than to that of the stress of liquids. This is caused by the presence of comparatively large structural elements (macromolecules of gelatine) in the solution which require a longer time for rearrangement.

Delayed elasticity is often observed together with relaxation when real bodies are being deformed. Relaxation causes elastic strain to become plastic strain whereas in delayed elasticity, the entire elastic strain does not originate instantaneously (as in ideal solids). A part of this strain develops with time, and therefore elastic strain attains the maximum value, which corresponds to preset stress only after a definite length of time. Delayed elasticity is, as a rule,

exhibited all the greater, the less homogeneous is the structure of a solid.

Let us again consider the mechanical properties of solid-like microheterogeneous and colloidal systems which possess true elasticity. Such systems are polycrystalline metals, diverse cross-linked dispersed systems, gels, concentrated soap solutions, substances of high molecular weight and their concentrated solutions which exhibit not only resilience, but also high elasticity.

The behaviour of all these systems at considerable strains is similar to that of ideally elastic bodies. But at strains which cause

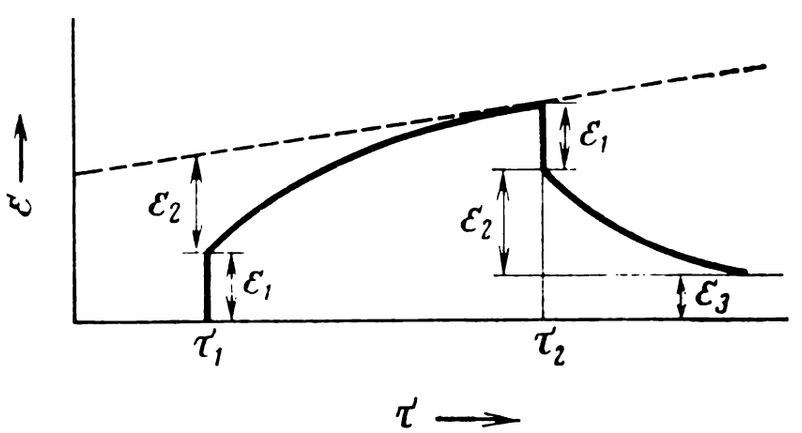

Fig. 10.8. Dependence of strain ε on time τ at constant stress for a system exhibiting instantaneous elastic strain, delayed elasticity, and flow

the destruction of a structural network, these systems can flow like viscous liquids, and their effective viscosity always decreases with an increase in the rate of flow or stress.

When these systems are being deformed, the phenomena of elastic (instantaneous) strain, delayed elasticity, and flow often occur together and produce a characteristic picture of a change in total strain with time (Fig. 10.8). As we may see, instantaneous elastic strain ε_1 develops under the action of a straining force, such as shearing stress P, applied to a system in instant τ_1. The instantaneous shear modulus $E_1 = P/\varepsilon_1$ corresponds to this strain. The system then begins to flow under the action of stress as a result of the irreversible rearrangement of structural elements. At the same time, delayed elasticity develops in the system and causes strain ε_2 owing to the reversible rearrangement of structural elements. Shear modulus $E_2 = P/\varepsilon_2$ corresponds to this elastic strain whose development is delayed. All this causes the curve in Fig. 10.8 to asymptotically approach a certain straight line which corresponds to the flow of the system. If the straining force is eliminated after a certain lapse of time in instant τ_2, elastic strain ε_1 will disappear at sonic speed. Then, strain ε_2, caused by delayed elasticity, will gradually disappear while strain ε_3, caused by flow (true relaxation), will remain irreversible.

Irreversible strain found under these conditions is sometimes not *true plastic*, but *apparent plastic* strain which originates because the shape of a deformed body is restored extremely slowly. In the latter case, permanent strain disappears either partially or completely as a result of such treatment of a body as heating or swelling in a solvent which causes structural elements to rearrange more quickly. It follows that a deformed body may have latent resilience after a load applied from without is removed. Resilience, i.e., the ability of a dispersed system to regain its original shape when a straining force no longer acts on it, shows that the inner structure of a system hinders the irreversible movement of its elements relative to one another.

DETERMINATION OF MECHANICAL PROPERTIES OF COLLOIDAL SYSTEMS

Rigid systems possessing sufficient mechanical strength can be investigated by ordinary methods of physico-mechanical analysis such as plotting a curve which characterizes the dependence of stress on strain, determining maximum stress in stretch or shear, finding relative and permanent strain, and so forth. In this case, account must be taken of only the rate of strain because the latter strongly affects the results.

Several special methods have been proposed for determining the mechanical properties of gels and other cross-linked dispersed systems which exhibit resilience. Let us consider only two of them here.

Tangential plate displacement method. This method, proposed by Veiler and Rehbinder, consists in the determination of the force needed to displace a plate which is immersed in a test system. The design of the device used for taking measurement is schematically illustrated in Fig. 10.9.

Rectangular riffled plate *3* is suspended on rigid thread *4* and fastened to spring dynamometer *6*. The plate is immersed in the dispersed system being investigated which is poured in cuvette *2* before the test. The cuvette containing the dispersed system is fastened to lifting stage *1*. As the table with the cuvette is lowered at a constant speed, the dynamometer spring stretches and shearing stress, being proportional to the extension of the spring, originates in the system. This stretch can be measured with microscope *5* which has an eyepiece micrometer or with a microscale.

Shearing stress P is calculated according to the extent of stretch of the graduated spring and force F which corresponds to this stretch by the equation

$$P = F/(2s) \tag{10.15}$$

where s is the lateral surface of plate *3*.

Maximum shearing stress θ which characterizes the strength of the structure of a system and corresponds to the greater force (when the system does not slip along the plate surface) is calculated by the equation

$$\theta = F_{max}/(2s) \qquad (10.16)$$

The given apparatus can be used to determine maximum shearing stress, the elasticity modulus and effective viscosity, to study relaxation, and to plot strain curves ε, P at different rates of strain.

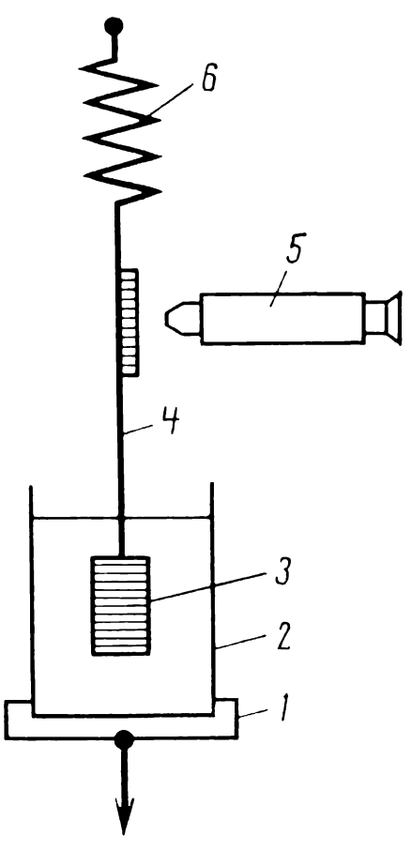

Fig. 10.9. Scheme of the apparatus proposed by Veiler and Rehbinder for determining the structural-mechanical properties of dispersed systems:
1—stage; 2—cuvette; *3*—riffled plate; *4*—rigid thread; *5*—microscope; *6*—spring dynamometer

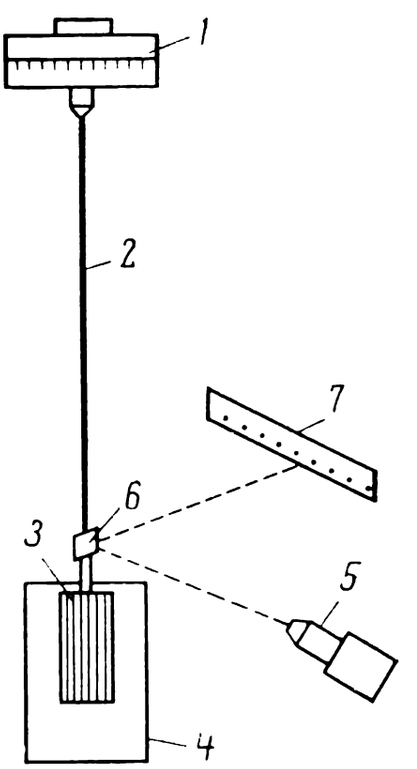

Fig. 10.10. Scheme of a torsional apparatus for determining the structural-mechanical properties of dispersed systems:
1—torsion head; *2*—elastic thread; *3*—riffled cylinder; *4*—cuvette; *5*—light source; *6*—mirror; *7*—scale

Cylinder torsion method. The method of determining resilient-plastic properties of cross-linked systems by the torsion of a cylinder which is suspended on an elastic thread and immersed in a test system was first proposed by Shvedov in 1889. Fig. 10.10 shows a diagram of the apparatus used for making a determination. The apparatus has torsion head *1* to which elastic thread *2* is fastened. Riffled cylinder *3* with mirror *6* is suspended on the thread. The cylinder is lowered into cuvette *4* containing the test system. As the torsion head turns by an angle α, the torque moment is relayed via the thread to the cylinder and causes shearing strains in the layer of the system that surrounds the cylinder. The cylinder also turns by an

angle β before equilibrium is established between the elastic stress of the thread and the resistance of the system being deformed. The difference ($\alpha - \beta$) gives the angle of torsion of the thread ω which corresponds to a force F that is set by the torsion head. The angle of rotation of the cylinder is measured by the shift of the light beam which is emitted by light source *5* and reflected by mirror *6* upon scale *7*.

This apparatus is convenient for studying the kinetics of the development of shearing strain after the application of preset constant stress, and the kinetics of the diminution of strain after the load is taken off.

Trapeznikov designed an apparatus known as the complex elastoviscometer. It allows the use of both various working cells (coaxial cylinders, cone, disc) and the diverse methods of investigation.

Methods of determining the resilient-plastic properties of cross-linked colloidal and microheterogeneous systems are considered at greater length in practical instruction manuals of colloid chemistry.

5. DEPENDENCE OF THE VISCOSITY OF COLLOIDAL SYSTEMS ON THE CONCENTRATION OF THE DISPERSED PHASE

The viscosity of a colloidal system is always higher than that of a pure dispersion medium. Proceeding from purely hydrodynamic notions, Einstein in 1906 derived an equation which established a relationship between the viscosity η of a system and the concentration of a dispersed phase:

$$\eta = \eta_0 (1 + 2.5\varphi) \tag{10.17}$$

where η_0 = viscosity of the dispersion medium;
φ = volume concentration of a dispersed phase.

Equation (10.17) can be used only if the particles suspended in a liquid are spherical solids, the concentration of a dispersed phase is comparatively low and particles do not interact. Moreover, in order to meet Einstein's equation, the system must be incompressible, liquid flow must be laminar, particle-liquid slip must be absent, and the particles must be large in comparison with the free path of molecules of the medium but small in comparison with the space where flow occurs.

The value of the numerical factor in Eq. (10.17) depends on the particle shape. Therefore, Einstein's equation in its general form can be written down as

$$\eta = \eta_0 (1 + \alpha\varphi) \tag{10.18}$$

where α is the factor which depends on the particle shape.

Einstein's equation is also often written as

$$(\eta/\eta_0) - 1 = (\eta - \eta_0)/\eta_0 = \alpha\varphi = \alpha\,(nv/V)$$

where η/η_0 = ratio of the viscosity of a colloidal system to that of a dispersion medium (relative viscosity);
n = total number of particles in a system;
v = volume of a particle of the dispersed phase;
V = volume of a system.

The quantity $(\eta - \eta_0)/\eta_0$, which characterizes the relative growth of viscosity of the dispersion medium when a definite amount of a dispersed phase is introduced into it, is called somewhat incorrectly specific viscosity, and is usually denoted by the symbol η_{sp}. It follows that

$$\eta_{sp} = \eta_{rel} - 1 = \alpha\varphi \qquad (10.19)$$

Thus, according to Einstein, there should be a linear dependence between the viscosity of a system and the content of a dispersed phase in it, but viscosity does not depend on the dispersity of a suspension.

Einstein's equation was verified experimentally by Bancelin with gamboge suspensions, by Odén with sulphur sols and, more substantially, by Ehrlich with the suspensions of tiny glass balls, spherical spores of fungi, and yeast cells. In all these investigations, the numerical factor at φ was about 2.5 if particles were spherical and the concentration of the dispersed phase was low. Deviations were observed when the particles were not spherical, the concentration of the dispersed phase in the suspension was considerably large, and electric or other forces acted between particles.

Effect of the anisodiametric nature of particles. When the particles of a suspension are rods, ellipses, or plates, the viscosity of a system is always higher than it should be according to Einstein's equation. This is because the liquid which gets into a volume (ellipsoid of revolution) formed around non-spherical particles that are in intensive Brownian motion becomes bound, as it were, with a particle. As a result, there is an apparent increase in the volume fraction of the dispersed phase in a system, and this causes an increase in viscosity.

It has been shown experimentally that the viscosity of a suspension having small anisodiametric particles, which are in intensive Brownian motion, increases proportionally to the square of the ratio between the large and small axes of the ellipsoid of revolution; the viscosity of a suspension having sufficiently large non-spherical particles, which are in slow Brownian motion, grows only in direct proportion to the ratio between the axes.

Theoretical calculations made by Kuhn, Simha and other researchers who used particles of the diverse shape as models are very complicated and sometimes ambiguous. Therefore, so far there is no general theory of the dependence of the viscosity of colloidal systems on the particle shape.

The viscosity of systems containing anisodiametric particles depends on the flow velocity. Elongated particles orient in flow where their rotary motion is hampered; as a result, the viscosity of a system decreases as the flow velocity increases. Such a phenomenon can be observed, for example, when measuring the viscosity of the V_2O_5 sol whose particles are highly anisodiametric.

Effect of the true concentration of a dispersed phase and solvation. The viscosity of a concentrated dispersed system differs from the viscosity calculated by Einstein's equation because mutually disturbing microflows originate in a liquid near particles and hinder the motion of a system. N. De Bruyne believes that, in this case, besides hydrodynamic interactions, account should be taken of mechanical interactions (the collision of particles, the formation of couples, and so forth).

At very low suspension concentrations, flow which originates around a particle hardly affects the velocity of flows near other particles and the velocity of liquid flow as a whole. But as the concentration of the dispersed phase increases, the effect develops and causes a deviation from Einstein's law.

The deviation of the viscosity of dispersed systems from that found by the Einstein equation can be also interpreted in terms of the solvation of particles. Solvation is the cause of the frequently observed dependence of viscosity on the dispersity of a system at the same volume concentration of a dispersed phase.

The effect of solvation can be represented in the following way. If a layer of the dispersion medium having a thickness of h sticks to the surface of a spherical particle whose radius is r, the effective volume of the particle (the volume of the particle together with that of the solvate layer) affecting viscosity is $4/3\,\pi(r + h)^3$. If the values of h are small as compared to those of r, we obtain $4/3\,\pi(r^3 + 3r^2h)$. Accordingly, when calculating the effective volume concentration φ of the dispersed phase, the quantity $4/3\,\pi(r^3 + 3r^2h)\nu$ (where ν is the numerical concentration), rather than $4/3\,\pi r^3\nu$, should be taken as the volume of the dispersed phase. If the true volume of the dispersed phase is taken as $\varphi_0 = 4/3\pi r^3\nu$, we obtain for φ

$$\varphi = \varphi_0\,(1 + 3h/r) \qquad (10.20)$$

Consequently, the quantity φ is greater than the volume φ_0 of the dispersed phase, and it is the greater, the smaller is a particle In other words, viscosity grows as the dimensions of sol particles

diminish. Such a growth in viscosity with an increase in the dispersity of a sulphur sol was observed by Sven Odén.

To take account of the solvation effect, Fikentsher and Mark proposed to modify Einstein's equation, introducing in it the effective volume (the volume of a system minus that of particles) rather than the total volume of a system, as it is done in the equation of van der Waals. Particles in a system are in a solvated state and undergo Brownian motion, circumscribing bodies of revolution; therefore, the volume of the dispersion medium which is energetically and sterically connected with particles should also be included in the volume of the dispersed phase. Eq. (10.18) will then be

$$\eta_{sp} = \frac{\alpha n v'}{V - nv'} \tag{10.21}$$

where v' is the volume of a particle together with the medium which is energetically and sterically connected with it.

The equation of Fikentsher and Mark explains why, in some cases, viscosity grows with the concentration of a dispersed phase more rapidly than it should according to linear dependence. Indeed, as the concentration of a dispersed phase grows in a solution, the quantity n proportional to it increases in the numerator and the quantity $(V - nv')$ simultaneously decreases in the denominator, and this causes viscosity to grow more rapidly than concentration.

Effect of interaction between particles. Einstein's equation cannot be applied in some cases to dispersed systems, on the one hand, owing to the forces of attraction which act between colloidal particles and cause the formation of loose structures including considerably large volumes of the dispersion medium. Such immobilization, i.e., a decrease in the mobility of a solvent, makes the viscosity of a system much higher than that calculated by Einstein's equation. Viscosity in such systems greatly depends on the flow velocity because it is structural viscosity engendered by the presence of loose three-dimensional networks in a system.

On the other hand, the inapplicability of Einstein's equation to colloidal systems may be caused by the forces of repulsion between particles which bear an electric charge of the same sign. According to Smoluchowski, the viscosity of sols having charged particles is higher than that of sols having uncharged ones. The growth in viscosity as a result of the presence of the electric double layer on the particle surface is known as the *electroviscous effect.*

Smoluchowski derived the following equation which connects the specific viscosity of a sol with the electrokinetic ζ-potential of the electric double layer of particles:

$$\eta_{sp} = 2.5\varphi\left[1 + \frac{1}{\eta_0 \gamma r^2}\left(\frac{\varepsilon\zeta}{2\pi}\right)^2\right] \tag{10.22}$$

where η_0 = viscosity of the dispersion medium;
γ = specific electric conductivity;
r = particle radius;
ε = dielectric constant.

The correction term in Eq. (10.22) may have a very high value. Calculations show that it may be ten times greater than the principal one for sols whose particle radius is 10^{-6} cm and electric conductivity is 10^{-4} ohm^{-1}·cm^{-1}.

According to Smoluchowski's equation, when electrolytes are introduced, the viscosity of colloidal systems should diminish as a result of both a decrease in the ζ-potential and an increase in the electric conductivity of the intermicellar liquid. When a sol is in an isoelectric state (at $\zeta = 0$), Smoluchowski's equation becomes Einstein's equation. However, when a colloidal system is astabilized by introducing an electrolyte into it (owing to a decrease in the forces of repulsion between particles in a sol), particles may aggregate to form structures and to produce structural viscosity, and this is not envisaged by Smoluchowski's equation. As a result, a diminution in the ζ-potential of sol particles under definite conditions may, besides not reducing the viscosity of a sol, even increase it.

Since Smoluchowski's equation includes the particle radius, the viscosity of sols whose particles bear an electric charge, unlike that of sols having uncharged particles, apparently depends on dispersity.

F. Booth in 1948 derived, for the electroviscous effect, an equation which considerably differs from Smoluchowski's one. According to F. Booth the magnitude of the electroviscous effect is much smaller than according to Smoluchowski's equation; it becomes negligible regardless of the value of the ζ-potential when the thickness of the electric double layer is very small in comparison with the particle radius.

11

SYSTEMS HAVING A GASEOUS DISPERSION MEDIUM

This and the subsequent chapters describe briefly systems having gaseous and solid dispersion media, and also systems having a liquid dispersion medium and a gaseous or liquid dispersed phase. They deal with systems whose particles are of colloidal dimensions, and also with microheterogeneous systems which are similar to them and have already been mentioned in Chap. 1.

1. GENERAL CHARACTERISTICS OF AEROSOLS

Colloidal systems having a gaseous dispersion medium are usually called aerosols although often their dispersity is less than the colloidal one; therefore, it would be closer to the truth to call them aerodispersed systems.

Aerosols differ from lyosols mainly by the rarefaction and lower viscosity of the gaseous dispersion medium. Therefore, Brownian motion occurs far more intensively in aerosols and their particles sediment considerably faster than in lyosols. Another distinction of aerosols from lyosols is that electrolytic dissociation cannot occur in a gaseous medium and, consequently, an electric double layer of ions cannot be formed around particles. Therefore, the science of aerosols developed independently.

Classification of aerosols. Aerosols are classified according to the state of aggregation of a dispersed phase, dispersity and the methods of obtaining them.

In conformity with the first principle, aerosols are divided into *fog*, i.e., systems having a liquid dispersed phase, and *smoke*, i.e., systems having solid particles. Dust having coarser solid particles should be related to smoke.

In practice, "smoke" often means an aerodispersed system which originates when fuel is consumed and contains both solid particles

of soot and ash and liquid particles of the products of fuel distillation and drops of water formed by the condensation of water vapour. Smoke, in which particles of a dispersed phase have adsorbed a considerable amount of moisture from the atmosphere, is known as *smog* (smoke + fog). Such systems are formed often in the atmosphere over industrial cities having a high content of moisture and smoke.

By dispersity, aerosols having a solid dispersed phase are divided into smoke with particles in the range of 10^{-7}-10^{-3} cm and dust with particles greater than 10^{-3} cm. Fog has rather large droplets, ranging from 10^{-5} to 10^{-3} cm.

By origin, systems having a gaseous dispersion medium, like all dispersed systems, are divided into *dispersion* and *condensation* aerosols. Dispersion aerosols are formed when solids are ground or liquids are sprayed; like lyosols obtained by dispersion, they have rather coarse particles and, as a rule, are polydispersed. Conversely, aerosols obtained by condensation from supersaturated vapours or by chemical reactions are highly dispersed systems whose particles have more uniform dimensions.

Dimensions and shape of particles. The dimensions of particles (in cm) of some typical aerosols are given below

Fog (H_2O)	5×10^{-5}
Stratified clouds	1×10^{-4}—1×10^{-3}
Rain clouds	1×10^{-3}—1×10^{-2}
H_2SO_4 (fog)	1×10^{-4}—1×10^{-3}
ZnO (smoke)	5×10^{-6}
Tobacco smoke	1×10^{-5}—1×10^{-4}
Flue gas	1×10^{-5}—1×10^{-2}
P_2O_5 (smoke)	5×10^{-4}—1×10^{-4}

The curve of distribution of particles in an aerosol, i.e., its content of particles of various radii, depends on the origin of the aerosol and on processes which occur in it later (aggregation, coalescence, isothermal distillation).

The shape of aerosol particles depends on the state of aggregation in which the substance of the dispersed phase is found. In fog, liquid particles are spherical. In smoke, they may have the most diverse shape; for example, they may be needles, plates or stars. In smoke, particles may form complex aggregates; in fog, the collision of droplets usually causes coalescence and the appearance of larger droplets.

As a result of the looseness (porosity) of aerosol particles, their density determined by conventional techniques is often lower than that of a constituting substance. This can be seen from the density of particles of some smokes obtained by various methods (Table 11.1).

Table 11.1. **Density of Particles in Smoke**

Substance	Density, g/cc		Method of obtaining smoke
	true	apparent	
Gold	19.3	0.2-8.0	Evaporation in a voltaic arc
Silver	10.5	0.64-4.22	Ditto
Mercury	13.6	0.07-10.8	Heating
Magnesium oxide	3.6	0.24-3.48	Combustion of metallic magnesium
Mercury chloride	5.4	0.62-4.3	Heating
Cadmium oxide	6.5	0.17-2.7	Evaporation in a voltaic arc

The dimensions and shape of aerosol particles are determined by ordinary microscopy, ultramicroscopy, and electron microscopy. To count particles in aerosols, it is expedient to use the flow microscope designed by Deryagin and Vlasenko (see Chap. 2).

The concentration of aerosols which can hardly be studied, such as the concentration of water in a cloud, can be determined by radar. A directed radio beam which "feels" space is emitted by radar as pulses at definite intervals and is recorded on the oscillograph screen. The radiation which was reflected after being scattered by a cloud is also registered by the oscillograph. The distance to the object is determined from the time taken by a radio signal to be sent and a scattered beam to be recorded; the concentration of the dispersed phase in an object is calculated by the intensity of the reflected beam because an equation similar to Rayleigh's equation describes radio waves scattering by small particles.

Optical properties. The optical properties of aerosols in general obey the same laws as those of lyosols. However, because of the difference in densities and, consequently, in the refractive indices of the dispersed and gaseous phases, the optical properties of aerosols, particularly light scattering, are very pronounced. Since aerosols have great ability to scatter light, they are used as smoke screens. Among all types of smoke, the P_2O_5 smoke has the greatest ability to scatter and reflect light; its masking ability is usually taken as a unit.

Molecular-kinetic properties. Aerosols are rarefied systems which have a small coefficient of internal friction of the dispersion medium. This is what determines their specific molecular-kinetic properties.

The motion of spherical particles, which are suspended in a viscous liquid (being regarded as a continuum) and are much larger than the molecules of the medium, can be described by the Stokes

equation

$$f = 6\pi\eta r u \tag{11.1}$$

where f = friction force of a particle;
η = viscosity of the medium;
r = particle radius;
u = velocity of movement of a particle.

Introducing the coefficient of viscous resistance of a particle, $B = f/u$, we obtain

$$B = 6\pi\eta r \tag{11.2}$$

To describe the motion of particles suspended in a gaseous medium, this hydrodynamic equation can be used only if the particle dimensions are considerably greater than the mean free path of gas molecules. Since, at atmospheric pressure, this quantity for air is about 10^{-5} cm, the Stokes equation can be applied only to coarsely dispersed aerosols whose particle radius is over 10^{-4} cm. When pressure is lower and, consequently, the free path is larger, the Stokes equation can be applied to aerosols at even lower dispersity.

For highly dispersed aerosols whose particle radius is below 10^{-6} cm, the motion of particles is described by the equation

$$f = 6\pi\eta r^2 u/(0.3502 \times 4.5\lambda) \tag{11.3}$$

or

$$B = 6\pi\eta r^2/(0.3502 \times 4.5\lambda) \tag{11.4}$$

where λ is the mean free path of gas molecules.

This equation is derived on the basis of concepts similar to those used in the kinetic theory of gases because, for small particles (or for low pressure) when $\lambda/r \gg 1$, aerosol particles move like gas molecules.

To describe the behaviour of aerosols having intermediate particle dimensions (10^{-6}-10^{-4} cm), transition formulas can be used, such as the Cunningham equation

$$f = 6\pi\eta r u \frac{1}{1 + A\lambda/r} \tag{11.5}$$

or

$$B = 6\pi\eta r \frac{1}{1 + A\lambda/r} \tag{11.6}$$

where A is a coefficient which approximates unity and whose value is determined experimentally.

As we may see, for high values of λ/r (when $A\lambda/r \gg 1$) in Eq. (11.3), the resistance force f is proportional to the square of the particle radius; for low values of λ/r (when $A\lambda/r \ll 1$), the Cunningham equation is transformed into the Stokes equation.

All the foregoing relates to the simplest case, i.e., to the motion of spherical particles. The relationship between the velocity of movement of particles and the acting force is more complicated for non-spherical particles.

Let us briefly consider Brownian motion in dispersed systems having a gaseous medium. This motion of particles in aerosols is strongly affected by sedimentation owing to the low viscosity and low density of the gaseous medium. This was not taken into account in earlier investigations, and therefore the values of average displacements in horizontal and vertical directions did not coincide. Moreover, owing to the low viscosity of aerosols, convection currents readily originate in them, and this also hindered the investigation of Brownian motion in these systems. But all these difficulties were overcome later as advanced methods of investigation were used; it was established that Brownian motion obeys the same regularities in aerosols as in lyosols. At present, Brownian motion in aerosols is studied by making a microscopic observation of sedimenting particles on which an electric charge is conferred. Charged particles, having sedimented by a certain distance, can be returned to the initial position by applying an appropriately directed electric field; thus, many measurements can be taken with the same particle, and this allows us to obtain precise results.

If an aerosol particle is not in Brownian motion, τ, the duration of its sedimentation by distance h, would be constant. But owing to this motion, a vertical constituent is added to the displacement of a particle. The time needed for a particle to pass distance h may be greater (if Brownian motion during sedimentation tends upwards) or smaller (if Brownian motion tends downwards) than the time taken for the particle to sediment. The large number of the values of τ_1, τ_2, τ_3 . . . obtained by such measurements for the duration of the sedimentation by the same distance h can be processed using the theory of Brownian motion. The diffusion coefficient calculated on the basis of the results thus obtained, taking account of the correction for sedimentation, coincides for oil fog, as Fletcher has shown, with the diffusion coefficient found for this system by other techniques.

It is important to take account of simultaneous diffusion and sedimentation processes when studying the behaviour of an aerosol which is confined to small space, or investigating filtration. For the sake of simplicity, suppose that an aerosol is confined to a sphere having radius R. In this case, the numerical concentration of the aerosol can decrease in two ways:

(1) particles in Brownian motion reach the vessel wall and adhere to it (since aerosol particles usually have no stabilizing factor, it may be assumed that every particle which collides against the wall remains on it);

(2) particles sediment to the bottom of a vessel.

The time τ_d needed for a particle, which is in the centre of a vessel, to diffuse to the wall can be found by the Einstein-Smoluchowski equation (see Chap. 3, Sec. 2) by substituting R^2 for Δ^2:

$$\tau_d = R^2/(2D) = R^2B/(2kT) \tag{11.7}$$

The time τ_s needed for a particle which is at a maximum distance from the bottom to sediment to it is determined by the equation

$$\tau_s = 2RB/(mg) \tag{11.8}$$

where m = particle mass;
g = acceleration of gravity (in this case, it is assumed that a particle sediments at a constant velocity of $2R/\tau_s$).

Since, for small particles, B, the coefficient of resistance of a particle, is proportional to the square of the radius whereas the particle mass is proportional to the cube of the radius, then $\tau_d \sim r^2$ and $\tau_s \sim 1/r$. It follows that the mean values of τ_d and τ_s, which are necessary for particles to adhere to the vessel wall and to settle to the bottom, depend differently on particle dimensions.

If particles are small, diffusion occurs more rapidly than sedimentation, and the destruction of an aerosol is caused mainly by the adhesion of particles to the wall, and not by their sedimentation to the bottom. If particles are large, an opposite phenomenon is observed, i.e., the destruction of aerosols is caused mainly by sedimentation.

Both very fine and very coarse particles rapidly disappear from an aerosol; the former, because of their adhesion to the wall, and the latter, as a result of their sedimentation to the bottom. Conversely, particles of intermediate dimensions stay longer in an aerosol. Particles for which $\tau_d = \tau_s$ are most stable. In equating Eqs. (11.7) and (11.8), it is easy to find the formula which can be used to calculate the mass of particles that stay the longest in an aerosol:

$$m_0 = 4kT/(gR) \tag{11.9}$$

All what we have said about the destruction of an aerosol in a confined volume relates to the destruction of systems having a gaseous dispersion medium as they pass through porous filters. The considerations evolved above explain also why mainly quartz particles whose dimensions correspond to mass m_0 are found in the lungs of persons suffering from silicosis. Presumably, crystals of larger and smaller dimensions remain almost entirely in the respiratory tract and do not reach the lungs.

Let us briefly consider the phenomena of thermophoresis, photophoresis, and thermoprecipitation which are connected with kinetic

properties and are characteristic of colloidal systems having a gaseous medium.

Thermophoresis is the motion of aerosol particles in a direction where temperature is lower. When the condition $\lambda/r \gg 1$ is met, i.e., when particles are small, thermophoresis originates because gas molecules collide at a higher velocity with the more heated side of a particle than with its less heated side; consequently, the particle moves towards lower temperature. If $\lambda/r \ll 1$, the cause of thermophoresis is more complicated, but a particle nevertheless moves in the temperature gradient field also towards lower temperature.

A quantitative theory of thermophoresis for small and large particles has been evolved by B. Deryagin, S. Bakanov, and Yu. Yalamov.

Photophoresis is the movement of aerosol particles when they are illuminated at one side; it is a particular case of thermophoresis. Photophoresis is more difficult to explain than thermophoresis because the distribution of temperature within the illuminated particle differs depending on its dimensions, shape, transparency, and the refractive index. For opaque particles, positive photophoresis is observed, i.e., particles move in the direction of a light ray. For translucent particles, negative photophoresis can be observed because the far side of a particle may be heated more strongly by rays which have refracted within it than the front side facing the light source. Small particles of some substances may exhibit negative photophoresis, and its large particles, positive photophoresis. Such a phenomenon occurs because, as the dimensions of a particle increase, light which has passed through it weakens to a greater extent and, consequently, the far side of the particle is heated less.

Thermophoresis and photophoresis are involved in the motion of atmospheric aerosols, e.g., when clouds are being formed. The thermophoresis of water droplets suspended in air originates when cold and warm air masses come into contact; photophoresis occurs as a result of the illumination of clouds by sun rays. The kinetic stability of atmospheric aerosols is rather peculiar. Owing to the small dimensions of droplets and the low settling rate (0.05-0.7 cm/sec), they are suspended, as it were, in the atmosphere, and the comparatively weak currents of warm air that rise from the earth are enough for the clouds to move as a whole over the earth. The droplets of clouds or fog fall as rain only when they become larger than the critical size as a result of coalescence or condensation.

Thermoprecipitation is the deposition of aerosol particles on cold surfaces; the particles deposit because they lose kinetic energy when they come into contact with such surfaces. It is this phenomenon which is involved in the deposition of dust on the walls and ceiling near furnaces, radiators, and lamps, and in pipes.

Electric properties. Electric double layers cannot originate around particles in systems having a gaseous dispersion medium. Nevertheless, aerosol particles under definite conditions may be charged although their charge is usually not high. The electric charge on particles in aerosols results either from the formation and subsequent interruption of the particle-particle or particle-surface contact or from the adsorption of gas ions on the particle surface.

In colloidal solutions, the value of the particle charge is determined by the selective adsorption of electrolyte ions and corresponds to the equilibrium between a particle and the surrounding medium; on the contrary, the charge of an aerosol particle is casual and depends entirely on the factors which cause it. For the same reasons, there is no strict relationship for aerosols between dispersity and the value of a charge. However, in general, it may be assumed that the charge of an aerosol particle is the higher, the greater are its dimensions. It has been found that the particles of aerosols of metals and their oxides, such as Fe_2O_3, MgO, Zn, and ZnO, usually bear a negative charge; conversely, the particles of aerosols of nonmetals and their oxides, such as SiO_2 and P_2O_5, are as a rule charged positively. The particles of NaCl, coal, and starch are charged positively; flour particles bear a negative charge.

Let us consider at greater length why electric charges originate on aerosol particles.

Suppose an aerosol particle has no charge and the adsoption on it of ions, which are always present in a gaseous phase as a result of the ionization of gases by cosmic or ultraviolet rays, is not specific. When such a particle collides with an ion, it adsorbs the ion and acquires a charge. Since the concentration of ions in a gas is low, these collisions are so rare that a few minutes may pass before another one. When the particle which has adsorbed an ion collides again with another ion, the particle charge may either increase or decrease, depending on the sign of the charge and the valency of the ion with which the particle has collided. As a result of such collisions, the particle may even change the sign of its charge or become electroneutral. Of course, ions captured by the particle are desorbed at the same time. Thus, a particle changes its charge from time to time, but the values of the charge in general deviate near the average neutral state. The variations of the charge of aerosol particles have the nature of fluctuations and are a reflection of the molecular-kinetic motion of ions and particles. Under such conditions, the probability W of acquirement of a charge by a particle is determined by the expression

$$W \sim \exp(-A/kT) \qquad (11.10)$$

where A is the work required for effecting fluctuation.

Experimentally verified calculations show that the charge of aerosol particles is usually very small and is rarely higher than the elementary electric charge by more than ten times. This has made it possible to establish the discrete nature of the ion charge and to measure the absolute quantity of the electron charge, as was done by R. Millikan.

Origination of electric charges on aerosol particles is more complicated when particles can selectively adsorb a definite type of ions, i.e., when the action of the adsorption potential is exhibited. In addition, a potential jump usually exists at the interface. A. Frumkin has shown that a positive electric potential of about 250 mV exists at the interface of the aerosols of water or snow owing to both the great dipole moment of H_2O molecules and their orientation. The potential jump at the interface may be caused also by *ballo-electrification*, i.e., the electrification of aerosol particles when they are being obtained by the dispersion method.

Owing to both the ability of the dispersed phase to adsorb ions specifically and the presence of a potential jump at the interface, aerosol particles adsorb various ions to a different extent and their average charge is not zero.

The particle charge causes phenomena which occur in large aerosol volumes, such as clouds. It has been found that the charge of water droplets in clouds approximates, in general, the potential of about 250 mV. In large atmospheric aerosol volumes, particles separate according to their dimensions and, consequently, their electric charge because particles having different radii sediment at a different rate. As a result, the electroneutrality of a cloud is upset and powerful electric fields originate in it; the lower part of the cloud usually acquires a negative charge, while the upper part is positively charged. Calculations show that, under such conditions, field intensity H in a cloud averages 100 V/cm. But when the polydispersity of the droplets of a cloud is considerable and convection currents are induced by the wind, much greater potentials may originate in a cloud, and they are the cause of lightning.

The charge of aerosol particles is determined by methods similar to those used for studying Brownian motion in these systems. First, the velocity of the free sedimentation of an aerosol particle is measured with great precision; then, the velocity of fall or rise of a particle in the electric field applied to it is determined, and the particle charge Q is calculated by the equation

$$u = u_s \pm u_e = \frac{1}{B}(mg \pm QH) \qquad (11.11)$$

where u_s = velocity of free sedimentation of a particle;
u_e = velocity of movement of a particle in an electric field;
m = mass of a particle;

g = acceleration of gravity;
H = electric field intensity.

The particle charge can be changed by the quantity ΔQ by ionizing the dispersion medium of an aerosol. A change in ΔQ is always the multiple of the quantity of the elementary charge $e = 4.8 \times \times 10^{-10}$ electrostatic units. The particle charge can be found when coefficient B is unknown, by applying a field having an intensity of H_0 at which the lifting force compensates for the particle weight. In this case, $u_s = u_e$. Substituting mg/B for u_s, and QH_0/B for u_e, we obtain

$$mg = QH_0 \tag{11.12}$$

from which Q can be found easily.

Aggregative stability. The electric charge of aerosol particles which is caused by the adsorption of ions is very small and sometimes practically zero. But can molecular adsorption layers originate on the surface of aerosol particles and are they capable of making aerosols aggregatively stable?

In early works, it is indicated that, at sufficiently high pressure, a polymolecular diffuse gas layer is retained on the surface of aerosol particles by adsorption forces. The presence of a gas shell was said to be, in particular, the cause of the non-deterioration of powders during storage, their ability to flow like liquids, and the non-wettability of solid aerosol particles with a liquid (it is known that smoke can pass through water, and particles of the dispersed phase do not remain in water). Some works even gave data on the amount of air adsorbed by an aerosol, and the amount of the adsorbed gas was usually much greater than that of the dispersed phase which had adsorbed it. However, works written in the last decades refute the possibility of adsorption of large gas quantities by aerosols, and therefore it is held that diffuse gas shells cannot be formed around their particles.

The surface of solid aerosol particles can undoubtedly be covered with a liquid film. For example, in ordinary smoke, such a film may consist of liquid distillates of fuel and condensed moisture. But it is very doubtful that liquid adsorption shells have a stabilizing action as indicated in some works. Since aerosol particles are surrounded by a gas and not by a liquid, disjoining pressure cannot be exhibited. In addition, surface tension at the liquid—gas interface always remains sufficiently high so that the free energy of a system can decrease when particles stick together.

J. Dalla Valle and R. Orr studied the effect of humidity on the coagulation of smoke and found that the rate of sedimentation of the aerosols of MgO, and especially NH_4Cl, considerably increased in a humid atmosphere. Microscopy has shown that aggregates of

particles become more compact in this case, presumably, because the condensed water film draws the aggregates together.

Thus, aerosols possess sufficient sedimentation stability as well as high dispersity, but are aggregatively very unstable, and coagulation always occurs in them. This explains the comparatively short lifetime of an aerosol. Most unstable are aerosols having the largest and the smallest particles: the former owing to the high rate of sedimentation of their particles, and the latter because of intensive Brownian motion which causes particles to collide and form aggregates.

Coagulation of aerosols usually occurs much faster than coagulation of lyosols due to more intensive Brownian motion in systems having a gaseous dispersion medium. The coagulation rate grows rapidly with the numerical concentration of an aerosol. Data on the rate of coagulation of aerosols as a function of concentration are given below.

Initial numerical concentration per cubic centimetre	10^{12}	10^{10}	10^{8}	10^{6}
Time required for reducing the numerical concentration by two orders	Fraction of a second	15-30 sec	30 min	Several days

It follows from these data that the numerical concentration per cubic centimetre cannot be higher than 10^{8}-10^{6} several minutes after an aerosol is obtained, regardless of its initial concentration. This is approximately 10^{8} times less than the numerical concentration of lyosols (e.g., a gold sol contains about 10^{15} particles per cubic centimetre). Thus, in both natural and industrial conditions very dilute aerosols are the most common.

The given data characterize the rate of aerosol coagulation only as the first approximation. Besides the frequency of collisions between particles, other factors also affect the rate of destruction of a system having a gaseous dispersion medium. For instance, the coagulation of aerosols is promoted by the polydispersity and anisodiametric shape of particles. Aerosols are destroyed more rapidly if they contain oppositely charged particles. On the contrary, aerosol particles scatter if their charge is of the same sign and sufficiently high.

Aerosol particles of a liquid with high vapour pressure resiliently rebound from one another when they collide. As Deryagin and Prokhorov have shown, this is caused by the evaporation of a liquid from the surface of droplets and, consequently, the formation of a diffusion-convection gas flow which hinders the coalescence of drops. It was confirmed by calculations that vapour pressure caused

by such evaporation is quite enough to infinitely hinder the coalescence of two liquid droplets which are in the immediate proximity (provided the evaporating liquid is replenished). Drops coalesce as soon as evaporation is prevented, for example, by saturating the surrounding air with the vapours of the same liquid. The aggregative stability of emulsions and suspensions does not increase owing to the dissolution of a dispersed phase in the dispersion medium, apparently, because diffusion in a liquid is very slow.

The rate of aerosol coagulation is, of course, affected by convection currents, mechanical stirring, and ultrasonic vibrations because all these effects make collisions between particles more probable.

The dimensions of particles can change in both aerosols and lyosols owing not only to coalescence and aggregation, but also to the isothermal distillation of a dispersed phase which makes big particles larger due to the evaporation of small ones. Under the appropriate conditions, the evaporation of mist droplets may cause an aerosol to become a homogeneous system, just as the dissolution of the dispersed phase of a lyosol causes the formation of a true solution.

Dependence of the properties of aerosols on the radius of their particles. Fig. 11.1 illustrates the dependence of the main properties

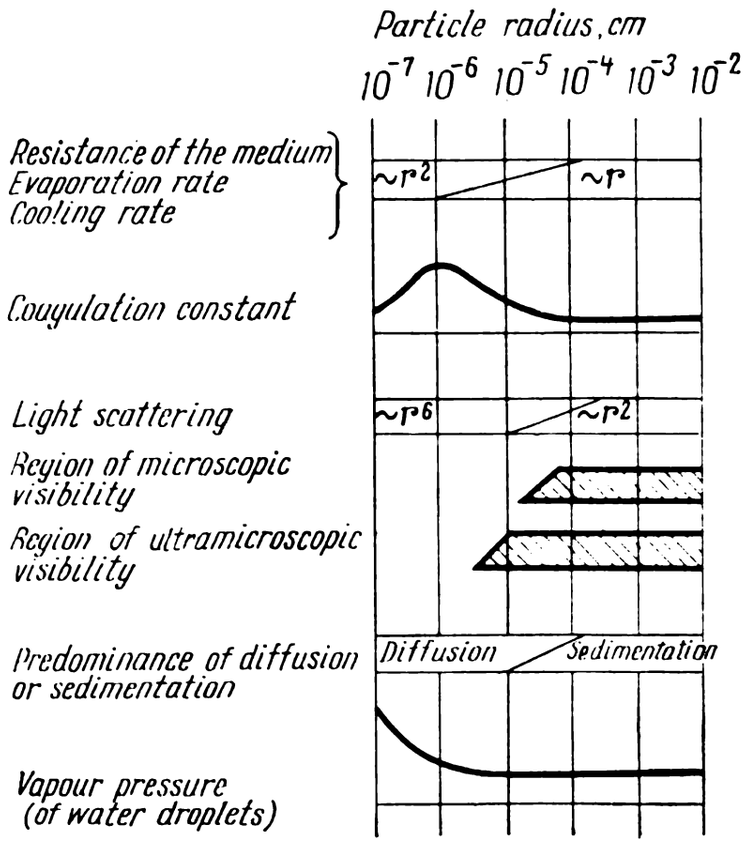

Fig. 11.1. Dependence of the main properties of aerosols on their dispersity (according to N. Fuchs)

of aerosols on their dispersity. The dependence of many properties, especially molecular-kinetic ones, on the radius of particles is more pronounced in aerosols than in lyosols.

2. POWDERS AND THEIR PROPERTIES

Powders are similar to aerosols by their properties; they can be regarded as aerosols with a solid dispersed phase, which have coagulated and formed a precipitate (aerogel). Coarsely dispersed systems, which are unstable with respect to sedimentation owing to the large dimensions of particles, should also be related to powders.

The dimensions of the primary particles of powders vary in a very wide range. The diameters (in μm) of particles of powders commonly used in technological processes and the food industry are shown below.

Soot	
gas channel black	0.03-0.09
gas furnace black	0.10-0.30
lamp black	0.30-0.60
Magnesium oxide	0.2-0.5
Titanium white	0.2-0.7
Zinc oxide	0.2-0.8
Lithopone (pigment)	0.3-0.8
Ferric oxide (pigment)	0.3-1.5
Barium sulphate	1-3
Chalk	
precipitated	1-5
ground	5-50
Kaolin	2-20
Starch	
rice	6-10
maize	15-25
potato	100-150
Wheat flour	
highest quality	50-200
third grade	up to 800
Cocoa	100-200

As the data show, only some types of soot have particles of colloidal dimensions; all the remaining powders are microheterogeneous systems.

The application of powders depends on the dimensions of their particles and, consequently, on their specific area. For instance, the brilliance of a colour and the coating ability of pigments (titanium white, lithopone, ferric oxide), the reinforcing action of fillers (soot, zinc oxide, magnesium oxide), and the palatability of powders used in the food industry (cocoa, flour) depend on their dispersity.

The dimensions of powder particles can be determined by microscopy, the sedimentation method, or screen analysis. The specific

surface area of powders is estimated by the adsorption of nitrogen on particles, the filtration of a liquid through a powder, or the suction of rarefied or non-rarefied air through a powder.

The most characteristic features of powders such as the ability to flow, to adhere and spray, fluidization, and granulation are presented below.

The ability to flow. Let us see how small particles move on the surface of a layer which consists of the same particles. Such motion is involved in the transfer of sand and soil by wind, the pneumatic transportation of loose materials, and so forth. It can be effected in three ways: (1) particles roll over the surface; (2) particles tear

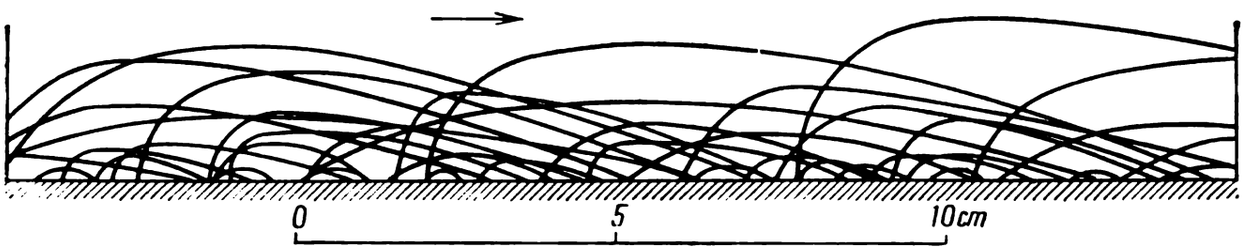

Fig. 11.2. Paths of jumping sand particles

away from the surface and immediately fall back on it, i.e., they move in "leaps"; (3) particles are transferred in an aerosol state. These types of particle motion can be observed in a wind tunnel with a thick layer of sand on its bottom. At a definite air velocity, particles that protrude from the sand layer begin to roll over until they are trapped in small depressions of the surface. If the velocity of air increases more sand particles will roll over and then stop, and so forth. These sand particles leap as they encounter other, larger particles which protrude from the surface. At a critical air velocity, a large part of sand particles moves in leaps; their paths are represented in Fig. 11.2.

It is still not quite clear how sand particles are torn away from the surface by an air current when they make a jump. If a particle jumps out of a laminar air flow which is moving near the surface, it is picked up by turbulent vertical pulsating air currents. Particles can tear away also when sand vortices break away locally from the surface (e.g., on sand or soil elevations). Sand particles occasionally ricochet from the surface, repeating their leap; sometimes, on falling, they are buried in sand and communicate their impulse to other sand particles which also begin to roll or jump. Thus, the transfer of sand or any powder resembles a chain reaction.

Sand particles whose radius is larger than 0.2-0.3 mm cannot jump and only roll when the wind velocity is below 10 m/sec; sand particles whose radius is larger than 1 mm do not move at all. There-

fore, the wind blows out smaller particles from polydispersed sand. The finest particles pass over to an aerosol state under the action of the air current and move over the sand surface in this form.

Once the transfer of sand or soil by wind has started, it spreads over a great distance. This process begins on small elevations under the action of vortices and accidental causes. Even low obstacles set up to combat wind erosion are effective because soil particles cannot jump over an obstacle, and the process is stopped.

For sand particles whose radius is larger than 50 μm, the critical velocity of "flow" over the sand surface is proportional to the square root of the particle radius. For sand particles whose radius is less than 50 μm, the critical velocity increases when smaller particles are involved in the process because of the molecular forces which operate between particles.

The values of the wind velocity at which sands of different dispersity begin to move are given below.

Radius of sand particles, mm	0.087-0.12	0.12-0.25	0.25-0.5	0.5-1.0
Critical velocity of the wind, cm/sec				
for dry sand	380	480	600	900
for sand having a moisture content of 2 per cent	600	750	950	1200

According to L. Danovsky, a noticeable transfer of snow begins when the wind velocity is 4-5 m/sec (on ice, when it is 2 m/sec) and rapidly grows as the wind intensifies. The acceleration of transfer of sand and snow with the intensification of wind makes these phenomena catastrophic during strong storms.

Adhesion. The ability of particles to adhere to surfaces is used when powders of insecticides and fungicides are applied to plants. In this case, particles tear away from surfaces (of leaves, etc.) arranged at different angles to the horizontal plane. The process accelerates with an increase in their mass, i.e., the adhesiveness of particles grows as their dimensions diminish. Adhesiveness depends also on the shape and nature of particles, on the material of the wall which determines surface tension, and on the plasticity of both a particle and the wall. The plastic deformation of contacting rough surfaces increases the contact area and requires a greater force for tearing away a particle from the wall. Therefore, particles of soft substances adhere better than those of solid substances.

The moisture content also influences adhesion. A water meniscus is formed in the place of contact between the wall and a spherical particle that has radius r and is being wetted; this meniscus draws a particle to the wall, as a result of surface tension, with a force proportional to $r\sigma$ (where σ is the surface tension of water). Since the

particle radius is considerably greater than the radii of curvature of the submicroscopic projections along which actual contact occurs, adhesiveness increases sharply with the moisture content. However, when particles adhere to the wall, electrostatic forces often originate; the moisture content promotes the neutralization of electric charges and thus decreases adhesiveness.

Spraying of powders and their fluidization (conversion into a state similar to a liquid state). These phenomena occur when coal dust is sprayed in furnaces by injector nozzles, powdery materials are pneumatically separated, mixtures of insecticides and fungicides are sprayed, chemical reactions are conducted in the fluidized bed, and so forth.

The following phenomena occur if a gas is passed at a growing velocity from underneath a layer of powder placed in a cylindrical vessel which has a porous bottom. At low flow velocities, powder particles do not move and thickness of the layer and the space factor Φ are constant. When the gas pressure gradient equals the gradient of "hydrostatic" pressure of powder, the resultant force among all the forces acting on a particle becomes zero, and the layer expands as the velocity of flow of the medium increases. Under these conditions, the layer of powder having coarse particles expands uniformly; contact between neighbouring particles is maintained, but the powder structure becomes more loose. In powders of greater dispersity, cohesive forces act between particles, and the powder layer no longer expands uniformly at sufficiently high velocities of flow of the medium, but disintegrates into aggregates having channels between them along which a considerable part of the gas flows.

Cohesive forces affect powder properties also under static conditions when air is not in motion. The bulk density $\Phi\rho$ of a coarse powder hardly depends on the particle dimensions because it is determined by the ratio of the weight of particles to the proportional to the weight force of friction between them. However, as the dispersity of a powder increases, intermolecular forces enhance the friction between particles, promote the formation of a looser structure, and therefore decrease bulk density.

The natural slope angle of powders also does not depend on the dimensions of particles in very coarse powders; it grows when powders having fine particles are used. As the layer expands, its fluidity (which is measured, for example, by the resistance offered to the layer by the stirrer revolving in it) increases by tens of times, and the slope angle diminishes considerably, i.e., the powder becomes similar to a liquid by its properties.

After the powder layer has expanded to definite dimensions (to 5-20 per cent of the initial volume, depending on powder properties), particles begin to move; the resistance of the layer to the

flowing medium diminishes owing, probably, to a decrease in friction between particles.

At a certain velocity of flow of a medium through a uniformly expanded layer of coarse powders, gas begins to bubble, just as when it passes through a liquid. As a result, the layer thickness continues to grow, but it fluctuates greatly. A powder in this state is very similar to a boiling liquid, and therefore such a layer is known as the fluidized bed. As the flow velocity increases, particles whose sedimentation rate is less than the velocity of flow of a medium over the layer, are carried away from the "liquid phase" (the fluidized bed) to the "gaseous phase" (aerosol). The concentration of particles in the aerosol phase grows until the boundary between the two phases disappears and the powder is wholly blown out by the gas.

The *aggregate fluidization* in fine powders is caused by cohesive forces. At low flow velocities, channels are formed in a layer and the bulk of gas passes through them. As the flow velocity grows, channels are destroyed, the layer is mixed intensively, aggregates continuously form and disintegrate, and particles are transferred to the aerosol phase. Since hydrodynamic forces grow faster than molecular ones as the particle dimensions increase, the best conditions for powder fluidization should be created at a certain average extent of dispersity. Indeed, the most uniform and complete fluidization is observed for powders having particles whose radius approximates 20-25 μm.

Since the friction of powders against a tube wall decreases as the particle dimensions increase (the action of molecular forces diminishes), the "flooding" phenomenon is observed in a layer of a coarse powder when the tube diameter is small: a gas raises the layer, forces its way through it, and then the layer falls again. If the flow velocity is gradually reduced and then stopped after a powder has been completely fluidized, the powder layer remains in an expanded state and has to be shaken in order to return it to the initial, non-expanded state. It follows that interparticle contact remains in the expanded layer; therefore, some authors are wrong when they assert that particles are surrounded by a "gas film" in this layer and, consequently, are not in contact with one another.

It is convenient to use the given technique for determining the values of the space factor Φ_{min} when a powder is in the expanded state. These values, which correspond to the greatest possible porosity or greatest possible volume of a given powder while interparticle contact is maintained, are among the important characteristics of powders. Table 11.2 gives the values of Φ_{min} and Φ_0 (corresponding to the non-expanded powder layer at rest) for some powders.

As the data in Table 11.2 show, the values of space factor decrease with a diminution of the dimensions of particles which are both at rest and in the expanded layer; this indicates the action of molecular

Table 11.2. **Values of Space Factors for Some Powders** (according to N. Fuchs)

Powder	Mean particle radius, μm	Φ_0	Φ_{min}
Glass balls	285	0.67	0.55
	115	0.66	0.54
Sand having spherical particles	185	—	0.58
	80	—	0.56
	42	—	0.53
	25	—	0.46
Sand having angular particles	160	—	0.50
	100	—	0.47
	42	—	0.43
	27	—	0.42
Ferric oxide	187	0.50	0.48
	100	0.48	0.44
	35	0.42	0.39

forces and, consequently, the contact between particles when a layer expands.

Some powders can be converted into an expanded state not only by passing a gas through them, but also by pouring them carefully. In such a state, many powders also possess great fluidity and are similar to liquids by their properties. Apparently, air between particles hinders their fall and makes their structure loose. In this case, gravity is not counterbalanced, and the fluidity of some coarse powders is probably caused by small molecular forces and, consequently, by low friction between particles.

Some powders raise dust when they are poured whereas others of the same dispersity do not. This ability of powders is often encountered in technology. It is caused by the action of cohesive forces between particles, increases with particle dimensions to a definite limit, and decreases as the moisture content of a powder grows. Therefore, hydrophobic powders (e.g., talcum powder) which cannot be wetted raise more dust than hydrophilic ones (quartz, limestone). Powders of soft, plastic materials raise less dust than powders of solids. Monodispersed powders raise more dust than polydispersed ones because the space factor and, consequently, the number of points of contact between particles in the latter are greater than in the former.

Dry granulation. This process is the opposite, in nature, of fluidization and spraying. Many powders can be transformed, as a result of minor mechanical stresses, into granules, i.e., large aggregates

which are usually spherical and disintegrate into powder on comparatively slight pressure. This process has been thoroughly studied with soot. Granulated soot has a smaller volume, does not raise dust, and possesses high fluidity which is convenient for transporting and processing it.

Soot can be granulated by shaking it on vibrating planes or by applying ultrasound to it. Granulation is more effective when soot is rolled in revolving cylinders. Voyutsky and his colleagues have shown that soot granulation by rolling is effective only when "nuclei" are introduced into powdery soot which can be obtained as small dense clumps when soot is passed through a narrow gap between rollers used in rubber production or by some other technique. Soot granules having a small diameter also can be used as nuclei in granulation. Granulation is caused also by any fine extraneous particles, such as plant grains and sugar crystals. However, too heavy particles, such as lead shot, cannot be used in granulation; apparently, the soot layer formed on the surface is destroyed under the weight of a shot when the latter collides with the cylinder wall or with another shot.

On rolling, powdery soot adheres, as it were, to the nuclei and then spherical granules are formed. The number of granules is usually equal to that of the nuclei and, by changing the ratio between them, one can obtain granules of any dimensions, even 1-2 cm in diameter. This reminds the formation of colloidal systems by condensation with the introduction of seeds, or nuclei, into a system. The strength of granules decreases as the ratio between powdery soot and nuclei increases.

Granulation is most effective at an average rolling speed. At very high speeds, the centrifugal force presses soot to the wall of a cylinder and soot is not rolled in it. At very low speeds, soot is not in rotary motion when a layer rolls on another and causes friction between particles that is required for granulation.

Since granules are formed when various powders are rolled, the granulation mechanism should be quite general. Particles of a powder interact with one another under the action of molecular forces to form aggregates. The sufficiently strong bond between particles may be caused either by accidental contact between them in more active sites or by contact along their plane facets, so that intermolecular forces can act in a larger area.

If a powder is stirred or poured at a moderate rate so as not to destruct aggregates, the latter accumulate gradually in the powder. Since these aggregates have a smaller surface curvature, particles adhere to them more firmly on collision, and the entire powder will be gradually converted into aggregates, i.e., granules. The aggregates are almost spherical because all the projections on their surface are smoothened out when the system is stirred or poured.

The formation of a firm bond between particles when a powder is being stirred or poured can be interpreted in a different way. To establish a contact and a firm bond, particles must overcome an energy barrier, such as the forces of adsorption of gas molecules by dust particles. Apparently, aggregates will be formed only upon successful collisions of particles which possess enough kinetic energy to overcome the energy barrier. Factors which cause elimination of adsorbed molecules should promote contacts and, consequently, the action of molecular forces. This is precisely what is observed in experiments: granulation improves when rolling is performed under vacuum and at elevated temperature.

A nucleus favours granulation because its mass is larger and its surface curvature is smaller than those of a powder particle. Since the mass of a nucleus is large, collisions are stronger; this helps to overcome the energy barrier and, consequently, causes agglomeration. A smaller surface curvature of a nucleus should also favour the interaction between it and a soot particle, i.e., the sticking of particles to a nucleus. Besides, a nucleus rolls between soot particles and causes their orientation which also promotes their sticking to a nucleus.

The main cause of the origination of a bond between granulated particles (contact between particles at certain sites) is confirmed by the growth in density and strength with the duration of rolling. Owing to jolts in rolling and slight impacts of granules, the number of contacts is greater and the system becomes more compact and strong.

Dry granulation of powders by moderate mechanical action should not be confused with other methods of packing powders and converting them into a non-dusting state: briquetting with the use of a binder, producing granules from a powder wetted with a small amount of a liquid, and so forth.

3. METHODS OF OBTAINING AEROSOLS

Aerosols, like other colloidal systems, can be obtained by condensation and dispersion.

Condensation methods. All these methods of aerosol formation are based on the condensation of supersaturated vapours. Vapours become supersaturated when either a system cools or vapour is formed by a chemical reaction.

Vapours may cool, supersaturate, and condense in various ways, e.g., when a gas containing vapours of a liquid expands adiabatically. Cumuli are formed in this way when warm masses of humid air rise to higher atmospheric strata. Cirri are also produced at high

altitudes by the condensation of water vapours, but, in this case, solid ice crystals are formed instead of liquid drops owing to low temperature. Cirri should thus be related to systems having a solid dispersed phase.

Vapours may cool, supersaturate, and condense also when they come into contact with a cold surface or mix with cold air. That is how fog is formed. In most cases, fog appears on a clear night when the earth surface cools rapidly as a result of thermal irradiation. Humid air invades an area having a lower temperature or comes into contact with the cooled earth; as a result fog droplets are formed in it.

Aerosols may be formed by various chemical reactions. For instance, smoke which contains products with very low vapour pressure is formed by oxidation when fuel is being consumed. As these products mix with colder air, they condense and form flue gas. Smoke is obtained also when phosphorus burns up in the air to yield P_2O_5 particles, when ammonia reacts with hydrogen chloride to yield NH_4Cl particles, when moist chlorine is exposed to light to yield hydrochloric acid (a photochemical reaction), and so forth. The oxidation of metals in the air upon various metallurgical and chemical processes often causes the formation of smoke consisting of particles of metal oxides, such as zinc oxide and magnesium oxide. Stable fog can be produced by such substances as SO_3 and HCl when they mix with air, and by $AlCl_3$ when it comes into contact with the humid air and reacts with water vapour to yield highly dispersed $Al(OH)_3$ particles.

A new phase must originate when aerosols are being obtained by condensation from supersaturated vapour. This is connected with great energetic hindrances, just as when any other system is being formed because the specific area is large at the beginning of formation of a heterogeneous system when its dispersity is very high. Therefore, when aerosols or lyosols are being formed, either supersaturation must be very high or condensation nuclei, around which the substance of a dispersed phase can be deposited, must be present or originate in a system. Such nuclei in the atmosphere may be fine salt crystals, ultramicroscopic dust particles, and other formations.

Let us at first consider how a new phase is formed in the absence of extraneous nuclei, using notions evolved by Volmer. For the sake of simplicity, let us take a case when a dispersed system with a liquid dispersed phase is being formed. If a system does not approximate a critical state, a new (liquid) phase cannot originate without great supersaturation because minute droplets, which are initially formed and are necessary for producing a fog with larger particles, possess a very small curvature radius; as a result, vapour pressure is very high at the surface of such droplets and they evaporate readily. A better understanding of this is obtained from the following considerations.

Vapour pressure p_r on the surface of droplets having radius r can be expressed by Thomson's equation

$$p_r = p_s \exp\left(\frac{2\sigma V_{mol}}{RTr}\right) \qquad (11.13)$$

where p_s = vapour pressure above the flat surface of a liquid;
V_{mol} = molar volume of a liquid.

According to Eq. (11.13), a liquid drop in an atmosphere of vapour having pressure p_s possesses higher pressure p_r than vapour pressure above the flat surface. Therefore it begins to evaporate, and the process accelerates as the radius of the drop diminishes since the difference between p_r and p_s is growing. Apparently, droplets can be in equilibrium only with supersaturated (with respect to the flat surface) vapours, and droplets of definite dimensions must correspond to any degree of supersaturation. But in order to originate in supersaturated vapour, such equilibrium droplets must grow out of smaller, unstable droplets, as a result of fluctuation of their dimensions. The process may occur readily when supersaturation is high.

It follows that, when extraneous nuclei are absent, a new phase may be formed only as a result of fluctuation, and the number of spontaneously originating nuclei, like the rate of formation of a new phase I_0, is proportional to the number of fluctuations. The probability of fluctuations is proportional to $\exp(-\Delta F/kT)$ (where ΔF is a change in the free energy of a system at a given fluctuation). The quantity ΔF is equal to work A which is required for isothermal and reversible nucleation. Thus,

$$I_0 = k \exp(-A/kT) \qquad (11.14)$$

Eq. (11.14) shows that the rate of formation of a new phase in the absence of extraneous nuclei is determined by the work required for spontaneous formation of aggregates of molecules whose pressure is equal to that of the vapour of a supersaturated system.

Volmer's theory has been confirmed experimentally by several authors. In particular, air saturated with the vapours of a given liquid was allowed to adiabatically expand in Wilson's cloud chamber. As a result, vapours cooled and, consequently, were supersaturated to a definite value. The chamber can be used to observe the beginning of condensation, i.e., supersaturation which corresponds to fog formation. To preclude the formation of droplets on extraneous nuclei, these nuclei are removed beforehand by multiple condensation from the gaseous phase. In this case, critical supersaturation, which corresponds to the beginning of the formation of a new phase, continuously grows to a definite limit.

Calculations based on the data thus obtained show that relative supersaturation, which corresponds to a noticeable spontaneous

formation of nuclei, is very high (200-300 per cent and even more). Such high degrees of supersaturation are rarely observed.

Thus, droplets are formed because the gaseous phase contains extraneous active centres which reduce work A. Such centres may be either ions or neutral liquid and solid particles which are present in a system.

The role of ions in the formation of a new phase in a gaseous medium can be proven using Wilson's cloud chamber. The chamber is filled with air and the vapour of a test liquid whose supersaturation is not enough to form a fog in non-ionized gas. Then the gas is ionized, for example, by high-energy particles (products of radioactive disintegration, cosmic rays), and fog tracks corresponding to the paths of particles can be seen in the chamber. They are caused by ions formed as a result of both collision between high-energy particles and gas molecules, and the condensation of vapours on these ions.

Let us consider the basic principles of the theory which explains the formation of a new phase on ions in vapours. When ions collide with a droplet of a liquid which is a conductor, they are uniformly distributed on the droplet surface and induce on it forces which tend to increase its area and, consequently, counteract and reduce surface tension; the work required for nucleation also decreases. The value of surface tension of a charged droplet can be found by the equation

$$\sigma = \sigma_0 - \frac{Q^2}{16\pi r^3} \tag{11.15}$$

where σ_0 = surface tension of an uncharged droplet;
r = radius of a droplet;
Q = charge of a droplet.

The pressure of saturated vapour above a charged droplet can be found from Thomson's equation by substituting the value of σ in it:

$$p_r = p_s \exp\left[\left(\frac{2\sigma_0}{r} - \frac{Q^2}{8\pi r^4}\right)\frac{V_{mol}}{RT}\right] \tag{11.16}$$

A diagram of this equation, which expresses the connection between the vapour pressure of a charged droplet and its radius, is given in Fig. 11.3. When ions are absent from a system, droplets cannot be formed without fluctuations in their dimensions (the pressure of surrounding vapour is always lower than that of vapour above an uncharged droplet). In the presence of ions and at certain vapour pressure, fluctuations are not necessary for the formation of droplets. Indeed, a charged droplet has vapour equilibrium pressure which is always less than the pressure of vapour in the surrounding medium. Thus, droplets will originate by condensation. Such a conclusion

is confirmed by the experimental evidence obtained with Wilson's cloud chamber.

At a pressure $p_a < p_{max}$ (see Fig. 11.3), droplets having radius r_a are formed spontaneously in a system which contains ions. Even at $p = p_s$, i.e., when there is no supersaturation, droplets having a very small radius r_0 are formed. In this case, curve *1* in Fig. 11.3 shows that droplets having a radius which corresponds to Eq. (11.16)

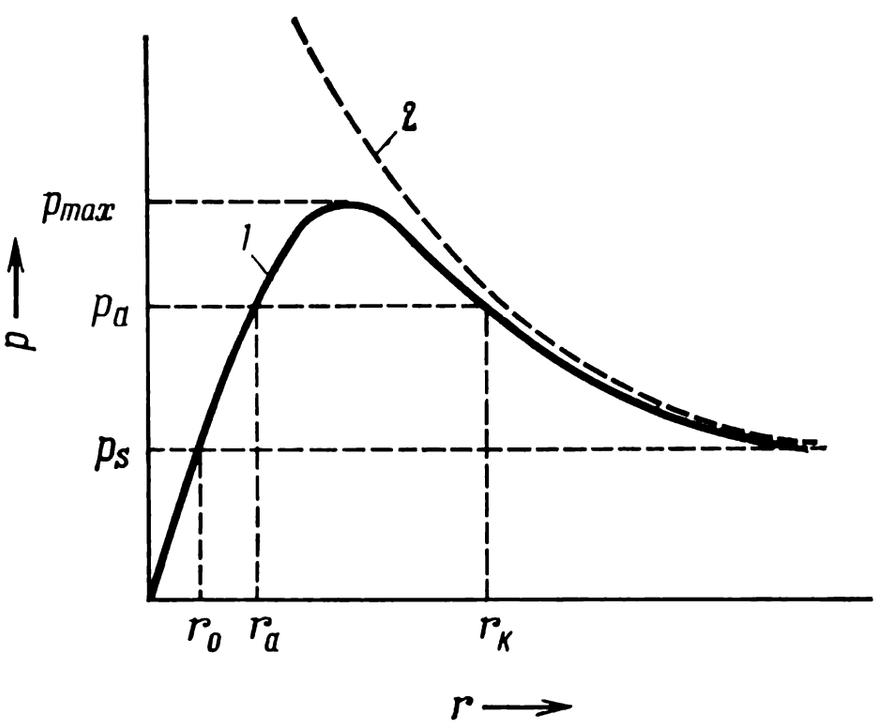

Fig. 11.3. Dependence of vapour pressure of a droplet on its radius:
1—for charged droplets; *2*—for uncharged droplets

are formed by condensation without fluctuations because a charged droplet of a smaller radius has a lower vapour pressure than that in the surrounding medium; it should grow as a result of condensation until the pressure of its vapour becomes equal to that of surrounding vapour. Apparently, a system then has the same number of droplets as it had of ions.

However, very fine charged droplets originating under these conditions cannot serve as nuclei for the formation of larger fog droplets because they cannot grow further. Indeed, curve *1* in Fig. 11.3 shows that, as the radius increases from r_a to r_k, droplets should grow when the pressure of their vapour is higher than that of vapour in the surrounding medium, and this is, of course, impossible. Therefore, droplets of radius r_k can be formed only by fluctuations. Of course, when the value of r_k is already attained, droplets may grow further without any hindrance, and each of them will then be a nucleus of a new phase.*

* For more details on the origination of droplets on ions, see A. Sheludko, "Kolloidna khimia" (Colloid Chemistry), Nauka i Izkustvo, Sofia, 1957.

The above-mentioned mechanism may be involved in the formation of a new phase on ions in vapours. However, it is apparently not significant in the origination of atmospheric aerosols because the atmosphere always contains nuclei which favour condensation at comparatively low supersaturation. Such nuclei may be fine salt crystals in the atmosphere over seas and oceans, ultramicroscopic dust particles, and so forth. The theory of condensation on nuclei has been elaborated inconsiderably yet because the structure and properties of nuclei are very complicated and diverse. It should only be noted that the nucleation rate should be proportional to the numerical concentration of nuclei.

Dispersion methods. The methods of obtaining aerosols by dispersion include the grinding and abrasion of solids, the spraying of liquids, and explosions. As a rule, lower dispersed and more polydispersed aerosols are obtained by dispersion than by condensation.

The method of spraying liquids by pressing them through special pulverizers and injector nozzles is used to uniformly deposit paints and lacquers on surfaces, to atomize liquid fuel, and so forth. Liquid sprays much easier if the liquid jet is charged up to several thousand volts.

In nature, aerosols containing drops of a liquid dispersed phase are obtained by dispersion of large masses of water in waterfalls.

4. METHODS OF DESTROYING AEROSOLS

Aerosols are destroyed if a dispersed phase must be separated from them, e.g., when valuable products are being collected from the smoke of metallurgical furnaces, or air or gases are being purified. Methods of destroying (coagulating) atmospheric aerosols have recently been used to make artificial rain or disperse clouds and fog.

In practice, particles of the dispersed phase are separated from gas by changing the velocity and direction of aerosol flow (inertial sedimentation), filtration, the action of ultrasound or the electric field, the introduction of nuclei, and coagulation.

The dispersed phase is separated from an aerosol by changing the velocity and direction of aerosol flow with the aid of centrifugal separators known as cyclones where an aerosol moves spirally in metal cylinders downwards.

Particles settle on cylinder walls while gas liberated from them rises along a pipe and is brought out of the cyclone. The motion of gas in a cyclone is schematically illustrated in Fig. 11.4. This technique is used only for destroying coarser aerosols which contain particles more than 3 μm in diameter.

Filtration can be used to separate much finer particles from a gas. Filters are used in gas masks to retain particles of poisonous fumes, to obtain sterile air, and so forth. There are mesh and fibre filters.

Mesh filters are used to retain coarser aerosol particles. They are made of one or several layers of cloth or a metal net. Their action is based on the mechanical retention of coarse particles, which do not pass through the mesh, and on the inertial sedimentation of particles. Mesh filters become more effective as they are clogged up with the dispersed phase being filtered off because the diameter of the openings through which an aerosol passes reduces as a dust layer is formed on the filter surface. Therefore, asbestos dust, especially effective in filtration, is sometimes deposited on cloth filters before they are used; in cleaning these filters, it is expedient to leave a part of the dust layer on their surface.

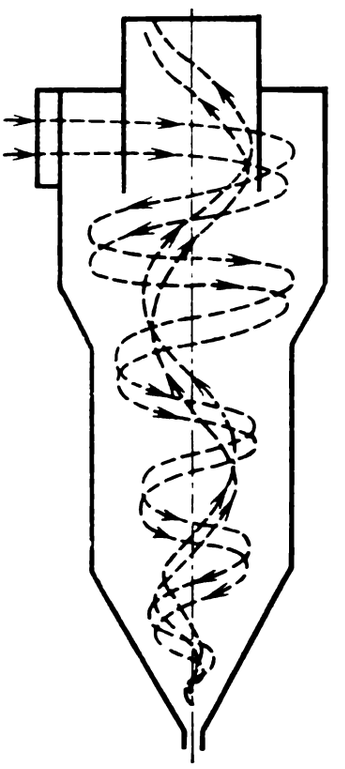

Fig. 11.4. Motion of gas in a cyclone

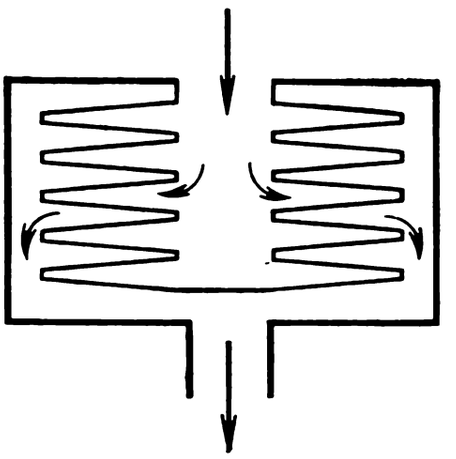

Fig. 11.5. Diagram of a filter with an expanded surface

Fibre filters are made of filter paper, cardboard, and some other fibrous materials. Owing to their great hydraulic resistance, the filters are used only at low velocities of aerosol flow. To increase their effectiveness, fibre filters are often made with an expanded surface. The design of such a filter is given in Fig. 11.5.

The nature of aerosol flow through a fibre filter is complicated, because flow constantly changes its direction as it rounds randomly arranged fibres. The work of fibre filters consists in inertial precipitation, the adhesion of moving particles to protrusions on the fibre surface (the engagement effect), sedimentation, and the diffusion of particles to the fibre surface with subsequent fixation. Diverse factors act differently on various phenomena which are the basis of separation of the dispersed phase in aerosol filtration. Inertial sedimentation increases with the dimensions and density of particles and the velocity of flow rate; diffusive sedimentation is promoted by a diminution in the dimensions of particles, but it does not depend on their density.

Of course, regardless of the predominant mechanism of sedimentation, filtration becomes more effective as the distance between fibres decreases, but then the resistance of a filter increases. Since inertial sedimentation predominates, especially in filtration at a high rate, the effectiveness of a fibre filter is determined by the tortuousness of pores and by the fibre radius rather than by the dimensions of pores.

Aerosol destruction by ultrasound has long been known, but it is beginning to be practically applied only now. The action of ultrasound on aerosols, like on lyosols, was interpreted in terms of different entrainment of particles having various dimensions by the vibrations of the medium in real polydispersed systems. As a result, small particles having a large vibration amplitude "comb", as it were, an aerosol, and therefore they collide sooner with larger, almost immobile particles. But this theory is contradicted by the fact that the smallest, most intensively vibrating particles remain uncoagulated in the ultrasound field.

According to another theory, ultrasonic coagulation is caused by attraction between particles which move in the ultrasound field. Such attraction may originate between aerosol particles if they move rapidly and parallel to one another in the same direction. Only a few seconds are enough for a fog to be coagulated by 90 per cent if it is moving in an ultrasound field. Large drops obtained by coagulation are easily separated from gas in ordinary cyclones.

Ultrasound is used to destroy smog containing sulphuric acid and other types of smog. Industrial devices with an efficiency up to 1000 m^3/min have been worked out for precipitating aerosols by ultrasound. Unfortunately, the most highly dispersed part of a fog usually remains uncoagulated in the ultrasound field. Moreover, ultrasound is scarcely effective for coagulating very dilute aerosol systems.

Destruction of atmospheric aerosols is also based on their coagulation. It is used in agriculture because the dispersed phase of atmospheric aerosols often separates as rain or snow, and in aviation

for artificially scattering clouds over airports. Atmospheric aerosols can be coagulated by strewing from a plane highly dispersed sand whose particles bear an electric charge opposite in sign to that of aerosol particles. V. Fedoseyev suggested to coagulate clouds and fog by spraying solutions of hygroscopic substances, e.g., concentrated solutions of calcium chloride, into an aerosol. Drops of this liquid entrap water drops, grow, and fall as rain. To destroy supercooled atmospheric aerosols, the fumes of silver iodide or lead iodide can be used; their particles are nuclei and cause the formation of ice crystals in clouds.

The dry-ice method of artificially scattering clouds and fog produced good results in practice. The method can be used when air temperature is below 0 °C and fog or clouds have a drop structure, i.e., for a supercooled aerosol. Dry ice (solid carbon dioxide having temperature of —79.8 °C) which is strewn in such an aerosol cools rapidly the air layer adjacent to it, and a large number of ice crystals are formed in it to become later crystal nuclei. These crystals grow quickly, even after they come out of the artificial cooling area because the pressure of saturated water vapours over ice is less than that over water. After attaining the critical dimensions, crystals separate from an aerosol as snow flakes. When this method is used, snow is formed in 5-7 minutes, and the area into which carbon dioxide was introduced is completely freed of fog in 15-30 minutes. The scattering process either does not occur at all or occurs very slowly when the amount of carbon dioxide introduced is too high, the water content of an aerosol is low, and supercooling is inadequate.

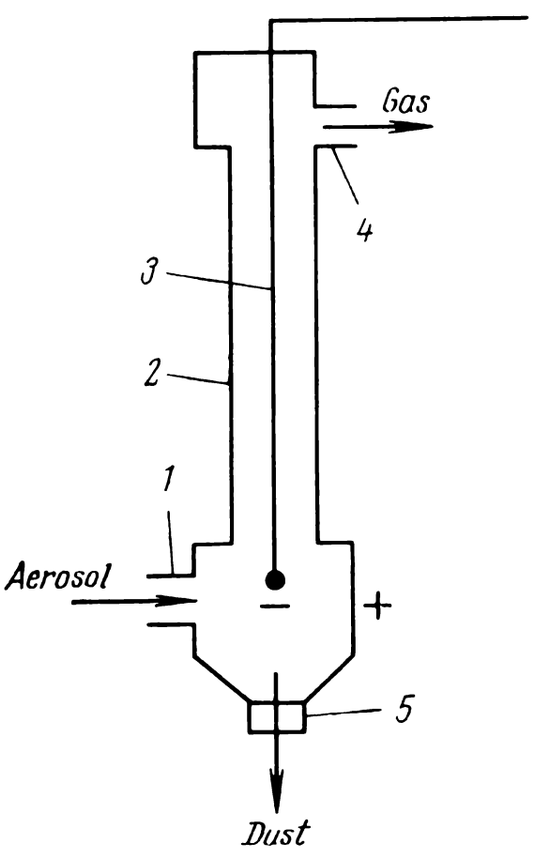

Fig. 11.6. Design of a battery cell of an electrostatic precipitator:
1, *4*—nozzles; *2*—anode; *3*—cathode; *5*—bunker

Aerosols can be also destroyed in an electric field of a high voltage. This method, worked out by F. Cottrell, is used in industry to remove dust from gases, to destroy smoke before it is discharged into the atmosphere, and for other purposes. Since aerosol particles are usually either weakly charged or almost electroneutral, a sufficiently large electric charge is conferred on them by passing smoke or fog between electrodes which create a field of a very high voltage. Un-

der such conditions, the corona discharge occurs; the cathode (which is a wire so that the charge would have the greatest density) glows and emits a great amount of electrons. The electrons ionize molecules of gas (air) which is between electrodes. The negative ions (anions) formed are adsorbed by aerosol particles and confer a sufficiently high charge on the particles to make them move in the electric field and deposit on the anode. The migration of particles to the anode is promoted also by static breeze which originates between electrodes.

The design of a battery cell of an ordinary electrostatic precipitator is schematically illustrated in Fig. 11.6. An electric field originates between cathode *3* (the negative corona electrode) and anode *2* (a metallic tube). A direct current of high voltage (70-100 kV) is supplied to the electrodes. An aerosol enters the cell through nozzle *1*. Under the action of the electric field and static breeze, aerosol particles which have acquired a negative electric charge migrate to anode *2*, collide against it, lose their charge, and deposit on the anode. Then, they fall down the tube and are removed from it via bunker *5*. If aerosol particles are liquid, after droplets have coalesced, the liquid continuously runs down the tube and is also removed via bunker *5*. Stripped gas leaves the cell via nozzle *4*.

There are electrostatic precipitators where the processes of charging and depositing particles are separated in space. In such precipitators, less products of air oxidation (nitric oxides, etc.) are formed, and therefore they are used for air conditioning.

5. PRACTICAL IMPORTANCE OF AEROSOLS

Aerosols play an important role in our life because they are widespread in nature and are used to a great extent in technological processes.

Natural aerosols, i.e., clouds and fog, are significant to meteorology and agriculture since they determine precipitation and, to a considerable extent, the climate of a region. Such natural phenomena as rain, snow, thunderstorms and rainbows are caused by atmospheric aerosols. The pollen of plants, the spores of bacteria and mould, and light seeds are transferred as aerosols in nature.

Aerosols are often encountered in industry. In metallurgical and chemical industries, a great amount of smoke is discharged into the atmosphere. For example, N. Peskov has estimated that the following amounts of various substances (in kg) are carried with smoke into the air at copper works when 10,000 tons of ore are being processed:

As_2S_3	26,900	Zn	2785
Sb_2S_3	1906	Fe + Al	8100
Cu	1907	Bi	400
Pb	2170	Mn	80

Apart from the fact that valuable substances which could be used in production are discharged with smoke, the latter pollutes the environment, destroys vegetation, and ruins our health. Smog is formed when the atmosphere of industrial towns has a large amount of smoke and air humidity is sufficiently high. That is why, for example, Tokyo has so many smoggy days per year.

In industry, aerosols are formed during operation of such machines as crushers, mills, rollers, and sieves. The dust being formed contaminates a manufacturing process, gets between machine parts which are rubbing against one another, accelerates wear, and creates working conditions which are detrimental to people's health. Dust containing very fine, sharp quartz fragments is particularly harmful. Inhalation of such dust for a long time causes silicosis, a serious illness which often results in death. When sharp microscopic fragments of quartz get into the lungs they destroy the tissue and promote to infect the organism with such diseases as tuberculosis. Similar diseases are caused by the aerosols of oxides of some metals, such as zinc oxide.

In coal mines, dust formation may cause great explosions. The danger of an explosion exists at all enterprises that process powdery materials which are capable of burning, but are quite safe in their ordinary form (flour, sugar, sulphur). The specific area of a dispersed phase and, consequently, its area of contact with air are enormous whereas the thermal conductivity of an aerosol which promotes local heating is low. As a result, the oxidation reaction occurs at a very high rate as the dispersed phase of an aerosol burns up, and this causes an explosion. Aerosol explosions are more dangerous than gas explosions because the transition of a substance from a solid or liquid state to a gaseous one is accompanied by a greater increase in the volume of a system than when gas reactions occur. In the Soviet Union, attention is paid to the purification of exhaust gases and the collection of valuable substances contained in smoke, and to dust removal at industrial enterprises.

We have dealt mainly with the negative aspect of aerosols formed under industrial conditions. However, in some cases, aerosols have a favourable effect, and they are specially produced. For example, solid or liquid fuel is sprayed to a state of an aerosol or a microheterogeneous system when it is fed into a furnace. Various surfaces and objects are coloured with an aerosol of a paint or a lacquer obtained by pneumatic spraying with pulverizers. Such a technique is used also when metal coats are applied to surfaces. In agriculture, insecticides, fungicides, and herbicides are sprayed to combat harmful insects, fungi, and weeds. Aerosols are used in medicine when drugs are inhaled and in warfare for blackout.

12

SYSTEMS HAVING LIQUID AND SOLID DISPERSED PHASES

In dealing with aerosols, we did not take account of the difference between aerosols having a liquid dispersed phase and those having a solid one because they are rather similar in properties. Now, let us consider separately lyosols having gaseous, liquid, and solid dispersed phases, since their properties are very diverse, in conformity with the classification accepted in Chap. 1.

To begin with, let us deal with sols having a solid dispersed phase because we are already acquainted with them. In the preceding chapters, we considered the properties of colloidal systems by taking these lyosols as an example. Therefore, only a few additional remarks will be made now on suspensions, i.e., systems having a solid dispersed phase and a liquid dispersion medium whose particles are larger than those of colloidal systems. Then, let us regard emulsions as they are similar to suspensions in properties, and, lastly, foams, i.e., systems which greatly differ from suspensions and emulsions. At the end of the chapter, let us briefly consider systems having a solid dispersion medium.

1. SUSPENSIONS

Suspensions of powders in a liquid are encountered in nature and technological processes more often than typical sols having a solid dispersed phase. When the moisture content is sufficiently high, suspensions include soils, ground, clay mortar used in ceramics, as well as cement grout and lime milk used in construction. Suspensions of pigments in organic solvents are used as oil paints and colour lacquers, suspensions of graphite and coal are employed for creating crystallization nuclei in order to preclude the formation of boiler scales. In chemical manufacturing processes, the technologist has to deal with suspensions when salts in a fine crystalline state are being obtained.

Suspensions simultaneously absorb and scatter light although their particles are larger than colloidal ones. Unlike opalescing sols, suspensions are turbid not only in incident light, but also in transmitted light. But suspensions, like sols, are capable of exhibiting flow birefringence.

Since their particles are rather large (they are visible under the microscope), suspensions are unstable with respect to sedimentation if the density of a dispersed phase is not very similar to that of the dispersion medium, and the viscosity of the medium is not too high. For the same reason, suspensions do not exhibit osmotic pressure and Brownian motion, and are incapable of undergoing diffusion.

Suspensions and sols having a solid dispersed phase greatly differ from one another in optical and molecular-kinetic properties, but they have much in common as regards aggregative stability. As a rule, particles of suspensions, like those of lyophobic colloids, have a double layer or a solvent sheath on their surface. The electrokinetic potential of suspension particles can be determined by macro- or microelectrophoresis, and its value is similar to the ζ-potential of particles of typical sols. Under the action of electrolytes, suspensions coagulate, i.e., their particles agglomerate and form aggregates. Under definite conditions, three-dimensional coagulation structures capable of undergoing syneresis are formed in suspensions, like in sols. When the appropriate conditions are met, suspensions exhibit thixotropy and rheopexy usually to a greater extent than lyophobic colloidal systems.

Suspensions are characterized by processes which either are not inherent in colloidal systems or occur in them differently. Such processes include sedimentation and flotation, which have been considered in the preceding chapters, and also filtration and colmatage.

Filtration of suspensions is determined by the dispersity and extent of aggregation of particles, and by the formation of a coagulation structure and its ability to undergo self-packing in the filtering precipitate. Therefore, filtration is a complicated physico-chemical process which is affected by all the factors that control the aggregation of particles and the development of coagulation structures. Another complicated process is colmatage, i.e., the "inwash" of very fine clayey or silty particles into soil pores in order to reduce the water permeability of such hydraulic installations as dams.

2. EMULSIONS

Heterogeneous systems known as emulsions are widespread in nature (milk, latex, etc.). They are easy to be prepared artificially (impregnation mixtures for making textiles water-impermeable, lubricants, margarine, cosmetic cream, etc.).

Conditions required for forming emulsions are similar to those needed for obtaining colloidal systems which have a solid dispersed phase and a liquid dispersion medium. Both liquids constituting an emulsion must be either insoluble or sparingly soluble in one another, and the system must contain a stabilizer which in this case is known as an *emulsifier*. Emulsions are the more stable with respect to sedimentation, the more similar are the densities of both phases.

Not too concentrated emulsions are characterized by the spherical shape of particles (droplets). As a rule, the dispersity of lyophobic emulsions is considerably less than that of sols having a solid dispersed phase.

So-called *critical emulsions*, i.e., lyophilic emulsions, should be distinguished from typical lyophobic ones. Critical emulsions are systems formed usually from two finitely miscible liquids (e.g., aniline and water, isoamyl alcohol and water) at a temperature which is almost consolute temperature, when surface tension at the interface becomes very low (about 0.01 erg/cm^2) and the thermal motion of molecules is enough for dispersing one liquid in another. As a result of such spontaneous dispersion, a very thin emulsion is formed, and the coalescence of droplets in it is counterbalanced by the tendency of both liquids to become uniformly distributed in the volume (see Chap. 8, Sec. 1).

Any critical emulsion is a thermodynamically stable equilibrium system which does not require an emulsifier. A critical emulsion can exist only in a very narrow temperature range; moreover, particles of the dispersed phase (droplets of a critical emulsion) are continuously formed in a system and disappear immediately, being similar to associates which are formed in a liquid when its density fluctuates.

Classification of emulsions. Ordinary lyophobic emulsions are classified according either to the polarity of the dispersed phase and the dispersion medium, or to the concentration of the dispersed phase in a system.

According to the first classification, there are emulsions of a non-polar or weakly polar liquid in a polar one (e.g., an oil-in-water emulsion), i.e., *first-order emulsions*, and emulsions of a polar liquid in a non-polar one (e.g., a water-in-oil emulsion), i.e., *second-order emulsions*. First-order emulsions are often denoted by o/w where the letter "o" stands for oil or some other non-polar liquid, and the letter "w", for water or some other polar liquid. Second-order emulsions are denoted by w/o, accordingly. There is a special class of emulsions of liquid metals (mercury, gallium) in water because both the dispersed phase and the dispersion medium act as polar liquids.

The type of an emulsion is established easily by determining the properties of its dispersion medium: the ability of an emulsion to

wet a hydrophobic surface; its possibility to be diluted with water; the ability of an emulsion to be coloured when a dye which dissolves in the dispersion medium is introduced; and the electric conductivity of an emulsion. An emulsion is of the o/w type if it does not wet a hydrophobic surface, is diluted with water, becomes coloured with a water-soluble dye (e.g., methylene blue), and exhibits rather high electric conductivity. Conversely, an emulsion is of the w/o type if it wets a hydrophobic surface, is not coloured with a water-soluble dye (or is coloured with an oil-soluble dye, e.g., Sudan III), and does not exhibit noticeable electric conductivity.

According to the second classification, emulsions are divided into dilute, concentrated, and highly concentrated or gelated ones.

Dilute emulsions are liquid-liquid systems containing up to 0.1 per cent by volume of the dispersed phase. A typical example of such systems is the emulsion of machine oil in a condensate which is formed when a steam engine operates. However, the term "dilute emulsions" is not accurate because it is applied not simply to emulsions which have a low concentration of the dispersed phase and are obtained, for instance, by diluting concentrated emulsions, but also to systems possessing characteristic properties.

To begin with, dilute emulsions greatly differ by their particle dimensions from concentrated and highly concentrated emulsions, having the highest dispersity. The diameter of droplets in dilute emulsions is about 10^{-5} cm, i.e., it approximates the dimensions of colloidal particles. Furthermore, dilute emulsions are usually formed without the introduction of emulsifiers into a system. Nevertheless, particles of these emulsions were found to exhibit electrophoretic mobility and, consequently, bear an electric charge. The charge originates on particles of the dispersed phase of such emulsions upon the adsorption of ions of inorganic electrolytes which may be present in a medium in a negligible amount. Some authors hold that, when extraneous electrolytes are absent, hydroxyl or hydrogen ions of dissociated water molecules may adsorb on the surface of droplets of such emulsions. Lastly, dilute emulsions are more similar than all the other emulsions to lyophobic sols. F. Powis worked with dilute emulsions and ascertained that they obey the Schulze-Hardy rule, and their particles have a critical electrokinetic potential. The aggregative stability of dilute emulsions is promoted, besides the charge, by the extremely low numerical concentration of these systems, as a result of which droplets collide very seldom.

Concentrated emulsions are liquid—liquid systems whose content of the dispersed phase reaches 74 per cent by volume (Fig. 12.1*a*). This is the maximum concentration for monodispersed emulsions of this class; it corresponds to the maximum possible volume content of non-deformed spherical drops, regardless of their dimensions. For polydispersed emulsions, the given limit is, of course, nominal

because small droplets in them can be arranged between large ones, as is shown in Fig. 12.1*b*.

Since concentrated emulsions are usually obtained by dispersion, their droplets are relatively large, being 0.1-1.0 μm and even more. Such droplets are visible under a microscope, and concentrated emulsions must be related to microheterogeneous systems. Droplets of concentrated emulsions are also in Brownian motion which is the

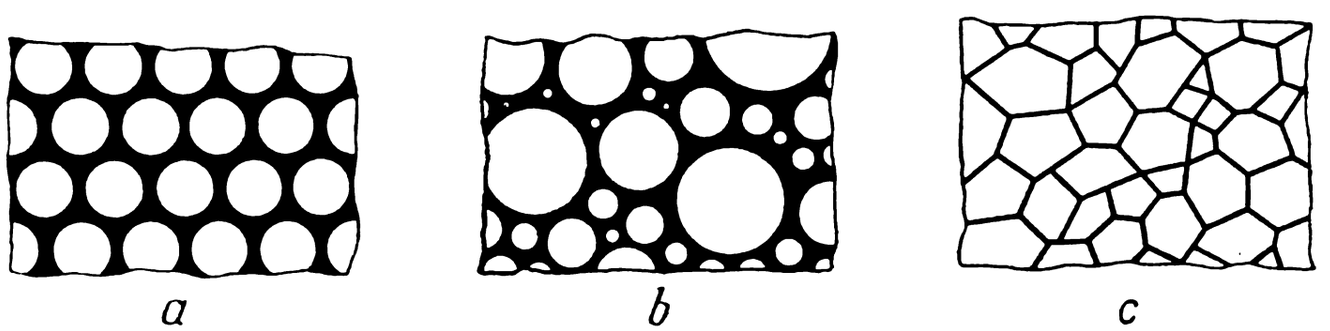

Fig. 12.1. Packing of droplets in emulsions having a high content of the dispersed phase:
a—monodispersed emulsion containing up to 74 per cent by volume of the dispersed phase; *b*—polydispersed emulsion; *c*—gelated emulsion

more intensive, the smaller are the droplets. Concentrated emulsions readily sediment, and sedimentation is the faster, the greater is the difference between the densities of the dispersed phase and the dispersion medium. Drops of the dispersed phase, if its density is less than that of the dispersion medium, rise to the surface.

The aggregative stability of concentrated emulsions is due to different factors, depending on the nature of emulsifier. Therefore, this will be discussed below when the types of emulsifiers are considered.

Highly concentrated (*gelated*) *emulsions* are liquid-liquid systems whose content of the dispersed phase is above 74 per cent by volume. Such emulsions are characterized by the mutual deformation of droplets of the dispersed phase; as a result, they become polyhedrons which are separated by thin films, i.e., interlayers of the dispersion medium. Under the microscope, such an emulsion resembles a honeycomb (Fig. 12.1*c*). Owing to the close packing of droplets, highly concentrated emulsions are incapable of undergoing sedimentation, and they possess mechanical properties similar to those of gels. That is why highly concentrated emulsions are sometimes called gelated ones.

Under certain conditions, highly concentrated emulsions can have a very high content of the dispersed phase and, accordingly, a negligible content of the dispersion medium. For example, an emulsion containing more than 99 per cent by volume of the dispersed phase can be obtained by emulsifying benzene in a 1 per cent solution of sodium oleate. In such highly concentrated emulsions, the

emulsifier solution is located as very thin films between particles of the dispersed phase. According to L. Kremnev's data, the thickness of such films may be 100 Å and even less, depending on the nature of an emulsifier.

Of course, specific mechanical properties of highly concentrated emulsions are exhibited the greater, the higher is their concentration. For example, o/w emulsions whose content of the dispersed phase exceeds 74 per cent by volume are still sufficiently mobile. But emulsions containing 95 per cent of hydrocarbon possess properties similar to those of a gel; for example, they can be cut with a knife.

Aggregative stability of emulsions and the nature of an emulsifier. Emulsions, like all the colloidal and microheterogeneous systems, are aggregatively unstable owing to an excess of free energy at the interface. The aggregative instability of emulsions is exhibited in the spontaneous formation of droplet aggregates with the subsequent coalescence of droplets. This may eventually cause the complete destruction of an emulsion and its separation into two layers; one layer originates from a liquid forming the dispersed phase in an emulsion, and the other, a liquid constituting the dispersion medium.

The aggregative stability of an emulsion is characterized by either the rate of its phase separation, or the lifetime of droplets which contact one another or the interface.

The first method is used to find the volume of the dispersed phase (or the dispersion medium) which has separated in a definite length of time after an emulsion was prepared. The kinetic curve which characterizes the stability of an emulsion can be obtained by plotting the values of the phase volume (expressed in per cent of the emulsion volume) on the ordinate, and the respective length of time, on the abscissa. Since the volume of a separated liquid phase is proportional to the height of its layer when an emulsion separates in a cylindrical vessel, the height of the layer can be used instead of the volume.

If the amount of a separated phase is proportional to time, the stability of an emulsion can also be characterized by its lifetime τ which can be found by the equation

$$\tau = H/u \qquad (12.1)$$

where H = height of an emulsion layer;
u = rate of phase separation.

The lifetime of an emulsion droplet is determined at the interface of both liquids. For example, if the lifetime of a benzene drop in water in the presence of an emulsifier is to be determined, a benzene layer is applied over a water layer, and a drop of water is carefully introduced with a pipette on the interface from the side of benzene

(Fig. 12.2*a*). Similarly, a drop of benzene is placed on the interface from the side of the water layer with a pipette having a bent tip (Fig. 12.2*b*). In both cases, the time taken from the moment of the deposition of a drop to its coalescence with the appropriate phase is registered. This time depends on the stability of an emulsion. If a water-soluble emulsifier is used when an emulsion is being obtained, the stability of a benzene drop at the interface in an aqueous solution of an emulsifier is always higher than that of a drop of the emulsifier solution in benzene. Thus, an o/w emulsion is formed when a

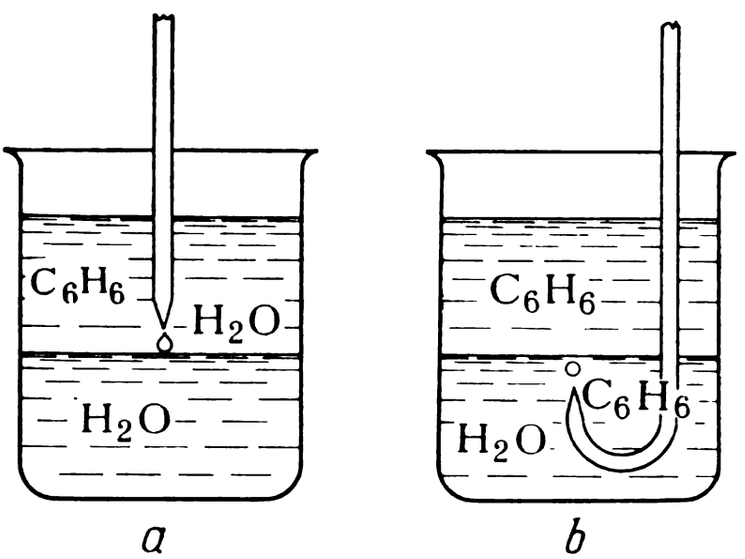

Fig. 12.2. Determination of the lifetime of emulsion drops

water-soluble emulsifier is used. Opposite results are obtained if a benzene-soluble emulsifier is used, i.e., a w/o emulsion is formed. Later, we shall explain why an o/w emulsion is formed in the first case, and a w/o emulsion, in the second.

The aggregative stability of emulsions is considerably affected by the nature of emulsifier and its content in a system. Thermodynamically, an emulsifier, while being adsorbed at the interface, reduces interfacial tension and, in some cases, can even cause the formation of equilibrium colloidal systems (emulsions obtained from coolants). Another explanation is that, when an emulsifier is present, repulsive forces (the energy barrier) appear between droplets at the interface. An emulsion becomes more stable when the concentration of an emulsifier in it is raised within certain limits.

The nature of an emulsifier determines not only the stability, but also the type of an emulsion. Hydrophilic emulsifiers, which dissolve better in water than in hydrocarbons, promote the formation of an o/w emulsion; hydrophobic (or oleophilic) emulsifiers, which dissolve better in hydrocarbons, favour the formation of a w/o emulsion (Bancroft's rule). This is quite clear because an emulsifier hinders the coalescence of droplets only when it is at the outside surface of a droplet, i.e., when it dissolves better in the dispersion medium.

Diverse substances can be used as emulsifiers: surfactants whose molecules contain ionogenic polar groups (soaps in the broad sense of the word), non-ionogenic surfactants, compounds of high molecular weight, and some powders. More or less concentrated emulsions cannot be stabilized by ordinary inorganic electrolytes because their ions are insufficiently adsorbed at the interface between a non-polar hydrocarbon and water.

The effectiveness of an emulsifier is denoted by a special number: the *hydrophile-lipophile balance* (HLB). If the HLB number is in the range of 3-6, a w/o emulsion is formed. Emulsifiers having an HLB number of 8-13 produce an o/w emulsion. Emulsion phases can be reversed by changing the nature of an emulsifier or its concentration. HLB is dealt with at greater length in Chap. 13.

The stabilizing action of soaps and soap-like substances on an o/w emulsion is said to be due to several stability factors.

The first factor is the electric charge which originates on the surface of emulsion drops that are stabilized by ionogenic soaps when the organic ions of soap are adsorbed. As a result, an electric double layer, similar to the one which exists on the surface of particles of typical hydrophobic sols, is formed. This double layer is what makes emulsions stable. Therefore, first-order emulsions, stabilized by ionogenic soaps, have all the properties inherent in typical hydrosols, i.e., the Schulze-Hardy rule is valid for them and emulsion particles' charge may be reversed with polyvalent ions, and so forth.

For an organic ion to be adsorbed, it must be adsorbed well by the dispersed phase, i.e., it must have a sufficiently long hydrocarbon chain. Therefore, o/w emulsions can be stabilized only by soaps of rather high molecular weight (alkaline salts of lauric acid and other fatty acids of a higher molecular weight). Alkaline salts of fatty acids that are lower members of a homologous series do not have emulsifying ability probably because the coagulating action of the ion of an alkali metal begins to predominate at high concentrations which are required for the adsorption of such soaps.

The second factor of stability of concentrated o/w emulsions is the formation of cross-linked gelatinous layers of an emulsifier on the surface of their droplets; these layers have high structural viscosity and strength, and are at the same time hydrated. This factor has been considered in detail by Rehbinder and Taubman in their works; it is even more important in the case of highly concentrated emulsions.

According to Taubman and his fellow workers, emulsions can be stabilized by several layers of microdroplets which serve as a structural-mechanical barrier and cover the surface of droplets of the main emulsion. Such microdroplets originate due to turbulence at the surface of the droplets of the main emulsion which has low interfacial tension.

The stabilization of w/o emulsions with soaps having polyvalent cations was said to be due mainly to the presence of a structural-mechanical barrier on the surface of emulsion droplets. The explanation that w/o emulsions are stable because an electric double layer exists at the interface seems at first sight to be untenable since the dielectric constant of the dispersion medium is low. However, it has been shown that emulsifier molecules may dissociate even in non-polar media (see Chap. 9, Sec. 2). Salts of polyvalent metals and organic acids in hydrocarbon media have dissociation constants of about 10^{-8}. For example, if the concentration of such a salt in benzene is 10 mmol/l, the concentration of ions in a solution will be about 10^{-10} N. Under such conditions, the electric double layer is, of course, very diffuse: its thickness would be several micrometres. Thus, the capacitance of the double layer in a non-polar liquid is very small, and a very low charge is enough to engender a considerably high surface potential. Thus, electrostatic repulsive forces can be involved in the stability of second-order emulsions, especially those which are not too concentrated.

The third factor, which can stabilize only second-order emulsions with soaps having a polyvalent cation, is the adsorption, on the surface of water drops, of polar ends of sufficiently long and flexible hydrocarbon parts of soap molecules that are dissolved in the outer non-polar phase of an emulsion and are capable of undergoing micro-Brownian motion. In this case, stability is apparently determined by thermal motion and the mutual repulsion of hydrocarbon radicals, i.e., by a factor which has an entropy nature.

Droplets of the polar dispersed phase of second-order emulsions may be also stabilized by an "armour" of granules made out of insoluble salts of alkaline-earth metals or hydrolysis products. This mechanism of stabilization is similar to that of the stabilization of emulsions with powdery emulsifiers which is considered below.

First-order emulsions are often stabilized with non-ionogenic emulsifiers whose diphilic molecules consist of a hydrocarbon radical and a hydrocarbon chain with polar groups. These groups (hydroxyls in most cases) are incapable of undergoing ionization and are arranged along the chain length (greater details on non-ionogenic emulsifiers are given in Chap. 13). The stability of o/w emulsions which are stabilized by non-ionogenic emulsifiers can be explained as follows. Diphilic molecules of an emulsifier are oriented at the interface in a way that the hydrocarbon parts are in the dispersed phase while polar, greatly hydrated groups are in water: they either form a sufficiently thick hydrate layer which causes disjoining pressure, or undergo micro-Brownian motion (entropy factor of stability).

The emulsifying action of both ionogenic and non-ionogenic surfactants is the more effective, the better balanced are the polar and non-polar parts of an emulsifier molecule between the two phases of

an emulsion. This means that the diphilic molecule of a good emulsifier must have affinity for both polar and non-polar media. Only then will emulsifier molecules dissolve not preferentially in one of the phases, but at the interface. The balanced nature of emulsifier molecules in the simplest case is determined by the length of a hydrocarbon chain, on the one hand, and the affinity of an ionogenic or polar group for water, on the other.

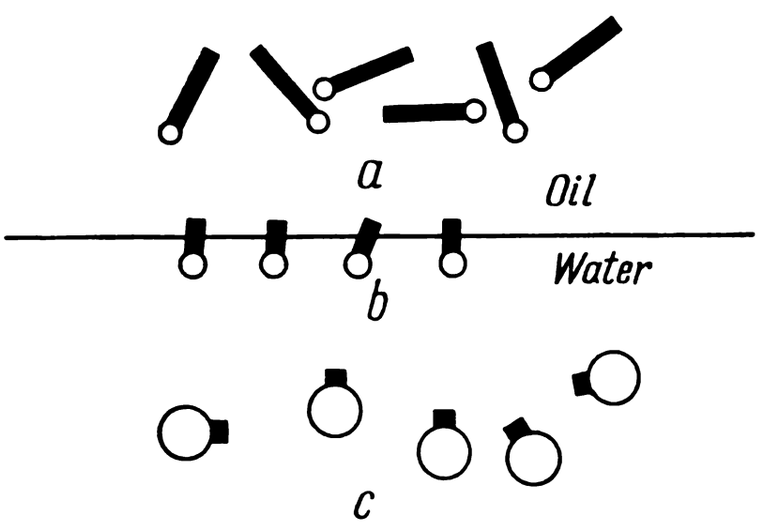

Fig. 12.3. Behaviour of differently balanced diphilic molecules of emulsifiers: *a*—molecules with a prevailing non-polar part; *b*—well balanced molecules; *c*—molecules with a prevailing polar part

The behaviour of differently balanced diphilic molecules can be seen from the diagram in Fig. 12.3.

A good balanced nature is what causes the best stabilizing action of soaps which contain 12-18 carbon atoms in a hydrocarbon chain. The order of emulsions depends on the balanced nature of molecules of an emulsifier which is used to obtain these emulsions. First-order emulsions are formed with emulsifiers in whose molecules the action of polar parts prevails over the action of non-polar ones, and which dissolve better in water. Conversely, second-order emulsions are produced with emulsifiers in which the action of non-polar groups of molecules predominates over that of polar groups, and which dissolve better in hydrocarbons.

The emulsifying action of substances of high molecular weight, such as gelatin, casein, polymethacrylic acid, methyl cellulose, and polyvinyl alcohol, and their action as protective colloids, can probably be explained by the entropy factor. It can also be taken that first-order emulsions, stabilized with protective colloids whose molecules contain ionogenic groups, are stable because an electric double layer is formed on the droplet surface upon ionization of the groups.

Let us now consider solid emulsifiers and the mechanism of their emulsifying action. Solid emulsifiers may be highly dispersed powders which can be wetted by both polar and non-polar liquids con-

stituting an emulsion. Such powders are clay, gypsum, ferric hybroxide, and soot.

When a polar liquid is shaken with a non-polar one in the presence of a solid emulsifier, its grains adhere to the interface; a larger part of the surface of emulsifier particles is in the liquid which wets them better. Thus, an "armour" is formed, as it were, on droplets, and it prevents them from coalescing. Of course, if a solid emulsifier is wetted better with water (e.g., kaolin), such an armour appears on

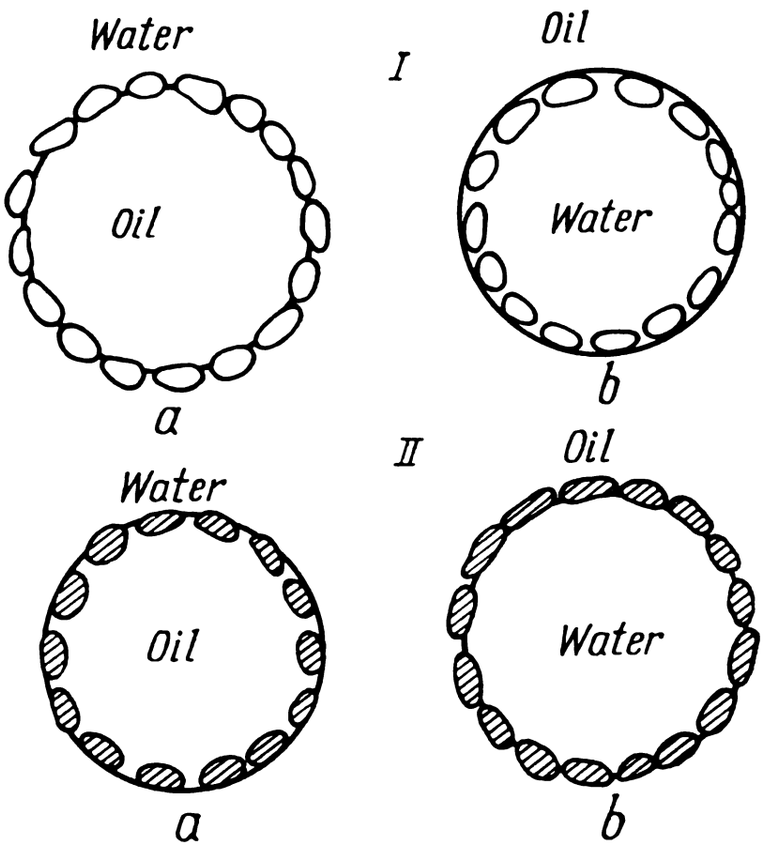

Fig. 12.4. Arrangement of small particles of a solid emulsifier at the interface when emulsion droplets are being formed:
I—hydrophilic emulsifier (kaolin); *II*—hydrophobic emulsifier (soot)

the side of the water phase, and an o/w emulsion is then formed. But if a solid emulsifier is wetted better with a non-polar hydrocarbon (e.g., soot) a w/o emulsion is formed. The foregoing is illustrated by a diagram in Fig. 12.4. In the cases of I*a* and II*b*, the granules of a solid emulsifier are outside the droplets, and therefore the emulsions are stable. In the cases of I*b* and II*a*, the granules of a solid emulsifier are at the interface within the droplets, and therefore such emulsions cannot be formed.

The presence of only a layer of a solid emulsifier on the droplet surface is not enough for a system to be aggregatively stable. The droplets of such an emulsion stick together on collision because there is always interfacial tension at the interface between a solid emulsifier and the dispersion medium. Apparently, the stability of emulsions

in this case is determined by the origination of either an electric double layer or a sufficiently thick solvent shell on particles of a solid emulsifier.

The foregoing classical concepts of the role of "armour" in the stabilization of emulsions with solid emulsifiers have been evolved by Taubman. He has shown that the high stability of natural emulsions stabilized with solid emulsifiers is determined by the joint action of a highly dispersed solid emulsifier and a surfactant, and that this stabilizing action is caused by the formation of a strong stabilizing shell. The structural-mechanical barrier was measured and compared with stability.

An emulsion can be stabilized by a solid emulsifier only if powder particles are smaller than emulsion droplets. At the same time, particles that are too small and are in intensive Brownian motion do not adhere to the droplet surface and do not form a protective layer. For example, o/w emulsions are obtained only if the emulsifier is a sol of As_2S_3 having moderately coarse particles. A highly dispersed As_2S_3 sol, like a coarse As_2S_3 precipitate, cannot stabilize emulsions.

Preparation and breaking of emulsions. Emulsions are prepared by shaking or stirring the dispersed phase and the dispersion medium, or subjecting them to vibration, when the emulsifier is present. Emulsors, stirrers, colloid mills, and ultrasound are used for emulsification. The coarse emulsions obtained are sometimes subjected to additional homogenization in homogenizers of various designs. In most commonly used homogenizers, droplets of a coarse emulsion are pressed through small openings under high pressure. When milk, for example, is processed in such homogenizers, the diameter of fat droplets diminishes from 3 μm to 0.2 μm, and the milk separates into phases much more slowly owing to its higher sedimentation stability.

Emulsification consists in dispersion proper, i.e., the formation of droplets of the dispersed phase in the dispersion medium, and their stabilization by adsorption on the emulsifier surface. Homogenization always consists in the formation of thin cylinders out of the dispersed phase that are very unstable and readily break down into droplets. We know from molecular physics that a liquid cylinder breaks down into droplets when its length becomes larger than its sectional circumference.

In emulsification, like in dispersion, droplets which have originated always coalesce to a certain extent because an emulsifier does not have time to be completely adsorbed on their surface, and their stability is less than that of the droplets in a prepared emulsion. Rehbinder has shown that two types of emulsions, o/w and w/o, are always formed in emulsification, and the emulsion which corresponds to the nature of the emulsifier "survives" because of a greater stability.

The effect of an emulsifier on the formation of an emulsion is more complicated when the emulsifier is capable of producing both o/w and w/o emulsions. In this case, the order of the emulsion being formed can be affected by the nature of the walls of a vessel and of a stirrer as well as by other objects with which an emulsion comes into contact. For example, if vessel walls are wetted only by one liquid, contact between an emulsion and the wall may reverse the type of an emulsion, and the liquid wetting the wall becomes the dispersion medium.

Emulsification depends not only on the nature of an emulsifier and the type of mechanical treatment, but also on temperature, the phase weight (or volume) ratio, and so forth. When all other conditions are equal, an emulsion of a lower concentration is more stable because a collision between two of its particles is less probable.

Thus, emulsification is a complicated process, and the technologist must be very experienced in order to prepare stable highly dispersed emulsions.

Besides mechanical dispersion, emulsions can be obtained by spontaneous dispersion whose mechanism has been considered in Chap. 8. Highly dispersed equilibrium systems obtained in spontaneous emulsification greatly differ in thermodynamic stability from ordinary emulsions whose aggregative stability is temporary. Surfactants used in spontaneous emulsification likewise cannot be regarded as typical emulsifiers because they are taken in amounts which change the bulk properties of a phase.

Spontaneous emulsification is involved in digestion and assimilation of food by an organism. For example, fat in the intestines is at first dispersed by surfactants of the bile (cholic acids), and then the highly dispersed emulsion is assimilated by the organism through the intestine wall.

The technologist's task is often not to obtain an emulsion, but to preclude its origination or destroy (*de-emulsify*) a system which has already been formed. Emulsions of the o/w type, obtained by means of ionogenic emulsifiers, are usually coagulated with electrolytes having polyvalent ions. Since such electrolytes produce water-insoluble compounds as they interact with the ionogenic group of an emulsifier, their introduction into a system is tantamount to making an emulsifier inactive. Emulsions obtained with the aid of ionogenic emulsifiers are often destroyed by introducing into a system an emulsifier which is capable of forming a second-order emulsion and thus neutralizes the initial emulsifier. Such an emulsifier is almost always formed when electrolytes having polyvalent cations are introduced into o/w emulsions stabilized with alkaline soaps because soaps with polyvalent cations, being then produced, promote the formation of w/o emulsions.

Emulsions stabilized by non-ionogenic emulsifiers are more dif-

ficult to destroy. Electrolytes break such emulsions only at high concentrations when they salt out rather than coagulate. Such emulsions can be destroyed more effectively by heating as a result of which molecules of non-ionogenic emulsifiers are desorbed from emulsion droplets, or the polar part of a molecule of a non-ionogenic emulsifier is dehydrated.

All emulsions can be broken by introducing a surfactant into a system; the surfactant forces out an emulsifier from the adsorption layer, but it is incapable of stabilizing the emulsion. This is precisely why some first-order emulsions can be destroyed by adding amyl alcohol to them. Emulsions can also be broken by centrifugation, filtration, and electrophoresis. Centrifugation or filtration concentrate emulsions. But droplets coalesce if emulsions have a high concentration of the dispersed phase and a low content of an emulsifier, and a system is thus destroyed. Voyutsky and his colleagues have worked out a method of continuously breaking emulsions of water in hydrocarbons by filtration. Droplets of the dispersed phase (water) are adsorbed on the filter, coalesce on its surface, and drip off (self-cleaning of the filter). Emulsions are destroyed when temperature rises because an emulsifier is desorbed from the droplet surface or dissolves in a dispersed phase.

Inversion of the emulsion type. Let us consider the so-called *phase inversion* which is characteristic of emulsions. When a large amount of a surfactant which stabilizes the opposite type of emulsions is

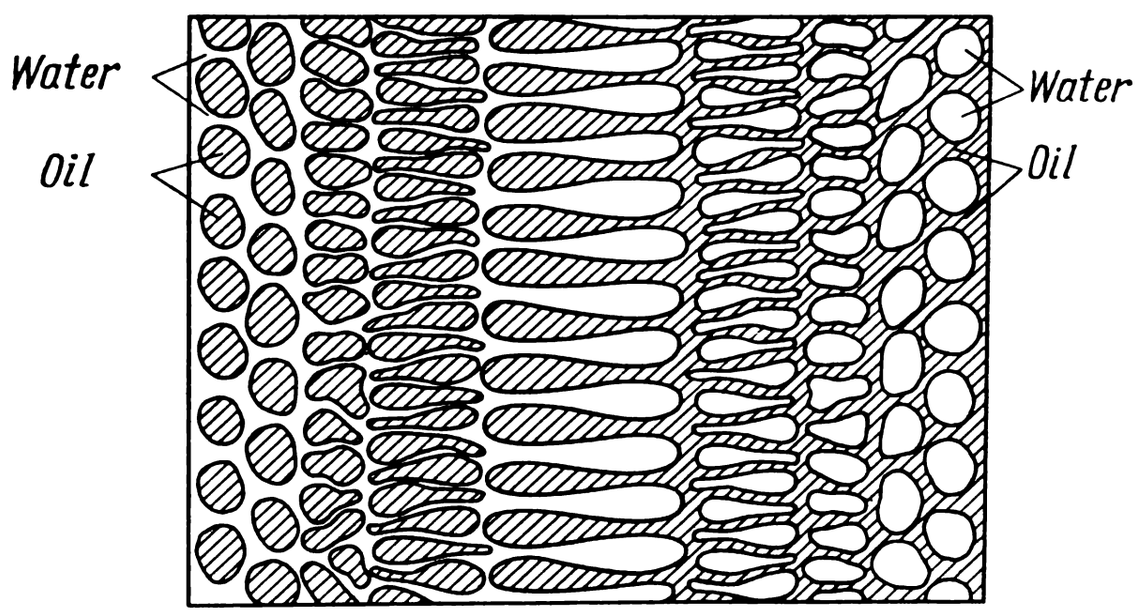

Fig. 12.5. Diagram showing inversion of the oil/water type of emulsion to the water/oil type of emulsion

introduced into an emulsion with intensive stirring, the initial emulsion may reverse, i.e., the dispersed phase in it becomes the dispersion medium, and vice versa. For example, an o/w emulsion, stabilized with sodium oleate, can be converted into a w/o emulsion by in-

troducing calcium oleate into the system with intensive stirring. The same phenomenon is observed when substances capable of changing the nature of an emulsifier are introduced into an emulsion, e.g., when calcium chloride is added to a first-order emulsion which is stabilized with sodium oleate.

Emulsions can be reversed under certain conditions by mechanical means acting for a long time. For example, butter is obtained by

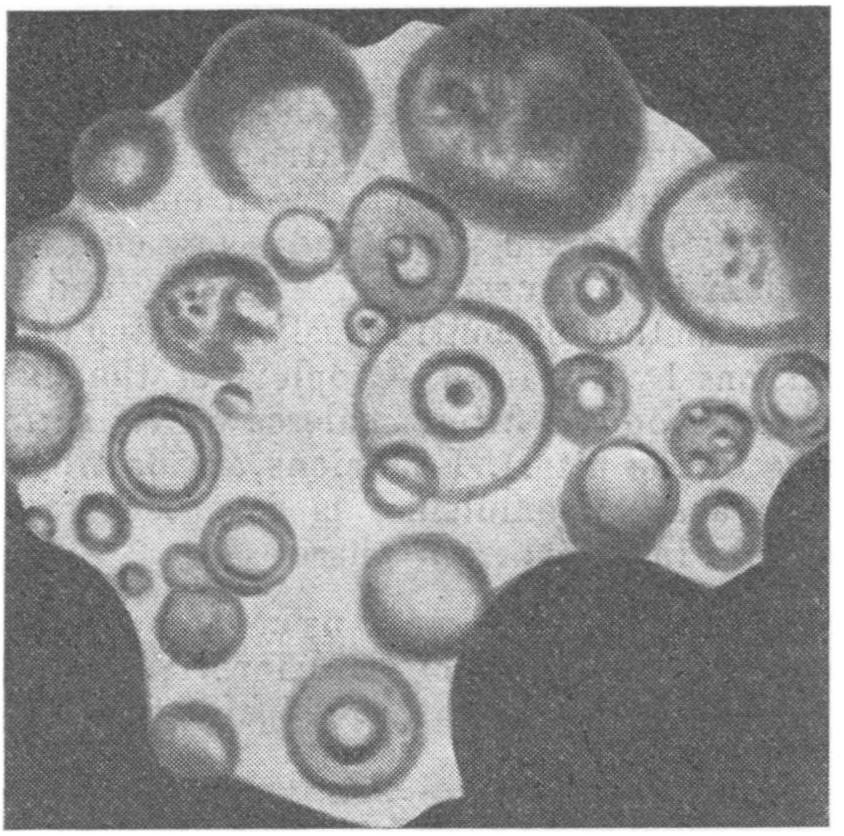

Fig. 12.6. Micrograph of a multiple emulsion

churning cream when an o/w emulsion (cream) becomes a w/o emulsion (butter) with a comparatively low content of water as a dispersed phase.

Microscopy reveals that, in phase inversion, droplets of a dispersed phase stretch out to become films, and then the films envelop the dispersion medium of the initial emulsion which consequently becomes the dispersed phase. Fig. 12.5 shows these stages in a left-to-right transition. As a result of an uneven distribution of an emulsifier in microregions of a system, "multiple" emulsions may originate when phases are reversed; for example, oil droplets of the first-order emulsion may contain minute water droplets. A micrograph of such a multiple emulsion is given in Fig. 12.6.

Practical importance of emulsions and emulsification. Natural emulsions include valuable vegetable and animal products. For example, milk is a fat-in-water emulsion stabilized with proteins.

Milk is a raw material of the dairy industry and is used to produce cream, sour milk, kefir, butter, cheese, and so forth. The egg yolk is also a natural emulsion.

In the food industry, apart from dairy products, margarine, mayonnaise, and various sauces are emulsions. In the pharmaceutical industry, many types of medicine are emulsions; as a rule, medicine introduced into an organism is a first-order emulsion whereas second-order emulsions are used for external application.

3. LATICES

Natural and synthetic latices are similar in properties to emulsions whose dispersion medium is water; these latices are used in the national economy for producing elastic films, pilot balloons, elastic porous materials, artificial leather, for making textiles water-impermeable, for impregnating the cord in the tyre industry, and so forth. Natural latices are the milky sap of rubber tree (*Hevea brasiliensis*). Synthetic latices are produced by polymerizing unsaturated hydrocarbons (butadiene, chloroprene, etc.) in an aqueous medium, and by copolymerizing two or even more monomers (butadiene-styrene latices, butadiene-acrylonitrile latices, etc.).

Latices, like emulsions, contain microscopic or ultramicroscopic particles (globules) which are almost spherical, and a stabilizer is adsorbed on their surface; the stabilizer is a compound of the protein nature for a natural latex, and it may be soap or other surfactants for synthetic latices. The substance of the dispersed phase of latices is raw rubber whose macromolecules are flexible hydrocarbon chains with or without polar groups. Such chains always contain unsaturated bonds which make it possible to vulcanize raw rubbers, i.e., to cross-link macromolecules by unsaturated bonds with sulphur or other vulcanizing agents.

Synthetic latices stabilized with soaps or soap-like substances are good models of ion-stabilized colloidal systems owing to the following properties.

The chemical composition of the aqueous phase (dispersion medium) of synthetic latices is rather simple, and the dispersed phase is usually a hydrophobic and sufficiently inert substance. Therefore, no reactions, except those in which a stabilizer participates, can be expected to occur on the particle surface when the systems are being astabilized. Solvation of the dispersed phase, which can affect the stability of a colloidal system, is undoubtedly absent from latices having a hydrophobic polymer. The spherical or almost spherical shape of particles precludes the effect of surface irregularity on their interaction; thus, two globules behave like two ideal balls when they collide. The dispersed phase of latices is

as a rule a dielectric, and no correction should be made for particle conductivity in electrophoresis. Owing to the high viscosity of polymers, globules of latices can be regarded as solid particles. This considerably simplifies the interpretation of experimental results because the surrounding liquid does not deform such particles. Synthetic latices can be obtained with almost any emulsifier. This is very convenient for studying the effect of the nature of stabilizing substances on latex properties. Latices are now widely used in research laboratories on account of their properties.

We will deal further only with latices which are stabilized with soaps or non-ionogenic surfactants, and are of general interest in colloid chemistry.

Although the relationship between the ζ-potential (electrokinetic potential) and the aggregative stability of lyophobic colloidal systems is a complicated problem, the ζ-potential is one of the most important characteristics of the stability of lyophobic colloids, particularly latices, as was indicated by Kruyt, Oberbeek, Hauser, and other authors.

Back in the early 1950's, Voyutsky and Panich studied the effect of such factors as the concentration of latices, the pH of a medium, and the valency of a coagulating ion on the stability and the ζ-potential of latices. Investigations were carried out with both non-dialyzed and dialyzed synthetic latices stabilized with ammonium oleate and ammonium naphthenate. Electrophoretic mobility was determined by macroelectrophoresis because the dependence of the ζ-potential on the concentration of the dispersed phase had to be determined. The ζ-potential was calculated by Henry's equation, and the numerical factor was selected in conformity with the known criterion $\varkappa a$, using Oberbeek's graphs.

When latices are diluted with a veronal buffer having pH 7.7, which is the same as the pH of these latices, the absolute values of ζ-potential at first grow, reaching 75-85 mV, and then drop when the content of a dry residue in latices is below 0.02-0.1 per cent. However, the values of the ζ-potential do not drop below —50 mV even at great dilution when it is difficult to observe electrophoresis.

According to Voyutsky, the initial growth in the negative ζ-potential when the system is diluted with a buffer having a constant ionic strength is caused by a diminution in the ionic strength of a system as a result of a decrease, per unit volume, in the number of globules which should be regarded here as polyvalent ions. W. Bowler, L. Munro, F. Sexmith have found a drop in the absolute quantity of the ζ-potential when latices are greatly diluted, which is caused by the desorption of a stabilizer from the globule surface. This interpretation was confirmed by the desorption of soap molecules from the surface of a dispersed phase to the interglobular liquid. However, this desorption is noticeable only when the content of a

dry residue in a latex is less than 0.02 per cent. In sufficiently concentrated, both non-dialyzed and dialyzed latices, over 99 per cent of soap is adsorbed, and the soap layer on globules is unsaturated.

Latices do not floculate or coagulate at high dilution, even when they are allowed to stand for two days. But highly diluted latices coagulate immediately when calcium chloride is added to them.

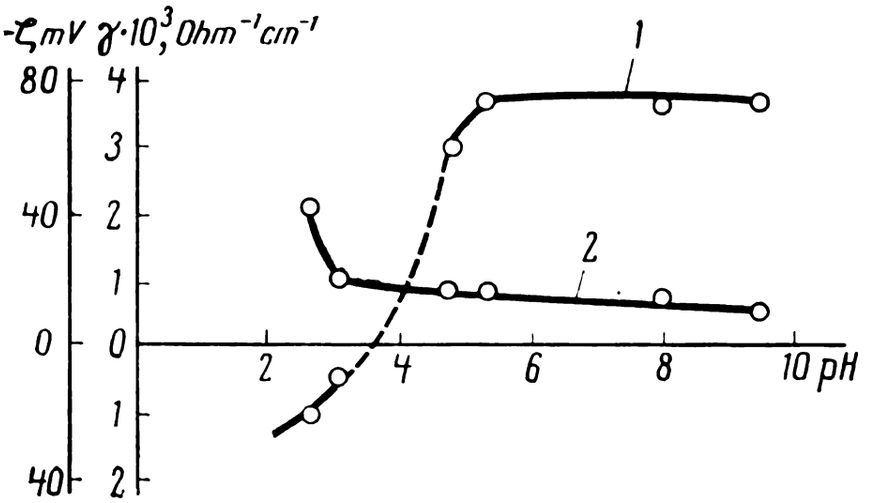

Fig. 12.7. Dependence of the ζ-potential of latex globules (curve *1*) and electric conductivity γ of the latex (curve *2*) on the pH of the medium

Therefore, the stability of highly diluted latices is determined not by the frequency of collisions between particles, but by their protection with a stabilizer.

Concentrated latices stabilized with soaps coagulate when 0.1 N HCl is being added to them. But the rapid addition of a sufficiently large amount of acid to latices, diluted to 3-4 per cent of the content of a dry residue in them, either does not cause coagulation or causes it partially. This phenomenon contradicts the common conceptions that latices stabilized with soaps (not with amphoteric substances) cannot be stable at low pH values. As a result of determining the sign of the charge on globules in acidified latices, it was discovered that they became positively charged.

Fig. 12.7 shows a change in the ζ-potential of globules of a dialyzed synthetic latex containing 2 per cent of a dry residue as a function of the pH of a medium when the ionic strength is 0.01. As the active acidity of a system increases, the ζ-potential does not change within a certain pH range; then, it begins to diminish as soap comes from the globule surface to a weakly ionized acid and is zero at pH 3.9. Finally, the ζ-potential acquires a positive value in strongly acidic media probably owing to the adsorption of hydrogen ions. The absolute value of positive potential of globules in an acid medium is much less than in an alkaline one; this is connected with the diverse nature and concentration of ions which stabilize globules in acid and alkaline media.

The aggregative stability of latices increases with the absolute value of the ζ-potential. It is well known that the stability of latices grows as the negative ζ-potential increases. But such a relationship is observed also for latices having positively charged particles. At pH 3.9, stabilized latices in an isoelectric state immediately coagulate. At pH 3.1, latent coagulation occurs which becomes obvious within a day. At pH 2.7, coagulation remains latent for 25 days. After charge reversal globules of latices are better adsorbed by

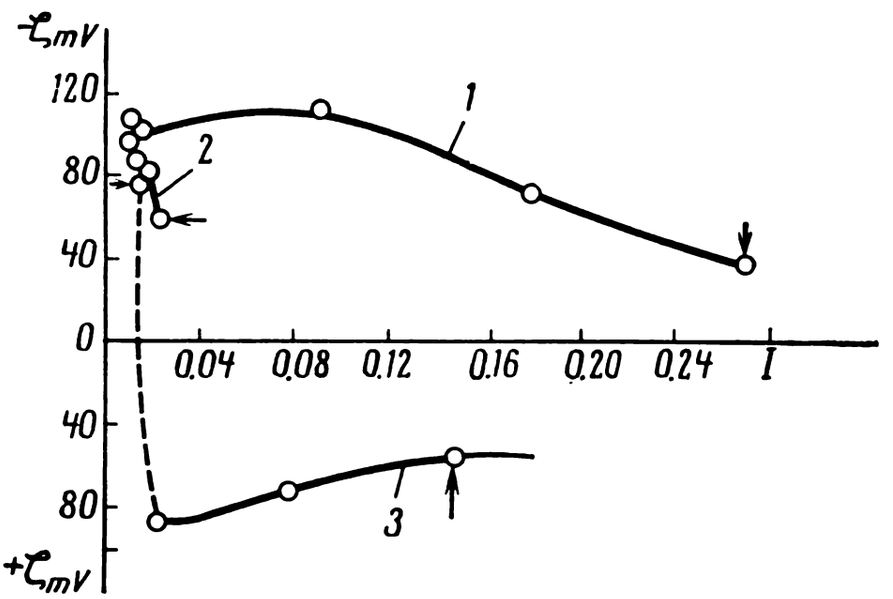

Fig. 12.8. Effect of the ionic strength *I* on the ζ-potential of the latex globules upon addition of different electrolytes:
1—NaCl; *2*—$CaCl_2$; *3*—$AlCl_3$

negatively charged surfaces, e.g., cotton fibre; consequently, they can be successfully used for pasting paper and cardboard and for impregnating textiles.*

In studying the effect of cations of different valencies on the ζ-potential of latex globules, it was found that latices having negatively charged particles obey the Schulze-Hardy rule, like all lyophobic colloidal systems. Fig. 12.8 gives the results of the electrophoretic investigations of a dialyzed synthetic latex containing 1 per cent of a dry residue. The terminal points on the curve, indicated with arrows, correspond to the maximum concentration of an electrolyte at which electrophoresis can still be effected. M. Bender and S. Maron have also observed an increase in the ζ-potential upon the addition of small amounts of sodium chloride, probably, due to the adsorption of anions present in a system by globules. The drop of the potential with an increase in the concentration of sodium chloride

* For details see: S. S. Voyutsky, *Fiziko-khimicheskie osnovy propityvaniya i impregnirovaniya voloknistykh materialov dispersiyami polimerov* (Physico-chemical Principles of Impregnating Fibrous Materials with Polymer Dispersions), Khimiya, Leningrad, 1969.

is caused by the compression of the electric double layer. That is also what causes a sharp drop in the potential when calcium and aluminium chlorides are added. As Fig. 12.8 shows, globule charge is reversed when large amounts of aluminium chloride are added.

Many authors hold that the structural-mechanical factor is cardinal in the aggregative stability of ordinary latices. But this viewpoint cannot be regarded as correct for latices stabilized with soaps. It has been shown that an emulsifier layer covers the surface of globules of stabilized latices only by 30-40 per cent. When the adsorption layer on the globule surface is considerably unsaturated, we can hardly speak about the presence of two-dimensional gels around particles and about their structural-mechanical properties. The stability of latices stabilized with soaps is determined mainly by the action of repulsive forces between electric double layers which originate when ionic atmospheres overlap. In this case, the stabilizing part of a soap molecule is its hydrated ionized groups whereas the hydrocarbon radical only fixes soap molecules at the polymer—water interface.

Stable latices can be obtained by means of such emulsifiers as Neckals which do not produce mechanically strong adsorption films. This is an additional proof that the electric double layer is the main factor causing stability of aqueous dispersions of polymers stabilized with soaps.

However, the structural-mechanical properties of the adsorption layer are also important to aggregative stability in general and that of latices in particular. Under definite conditions, when a sufficiently strong and thick layer of a hydrated stabilizer is formed on the particle surface, the structural-mechanical properties of the layer can determine the stability of a system.

According to R. Neiman, the electric double layer is being replaced with well-developed hydrate shells on the particle surface as the density of adsorption layers increases. Thus, systems stabilized by the electric double layer are replaced with systems whose stability is caused by the structural-mechanical barrier. In other words, the stabilization mechanism changes not only quantitatively, but also qualitatively, as adsorption by the surface of latex globules increases. An energy barrier which hinders coagulation is different; it approximates Rehbinder's concepts of the formation of cross-linked gelatinous layers of an emulsifier. In this case, the electric charge of an electric double layer either diminishes or disappears altogether owing to the close contact between ionogenic groups and a growth in the ionic strength. According to Neiman, the non-electrostatic nature of a stabilizing barrier here is also confirmed by the fact that the coagulation of adsorptively saturated latices does not obey the regularities characteristic of latices whose particles bear an electric double layer. Apparently, there is a different, non-electro-

static mechanism of stabilization which involves the structure and hydration of closely packed saturated layers of an emulsifier.

Non-ionogenic surfactants whose molecules contain several non-ionogenic polar groups, e.g., hydroxyls, are widely used now. The hydrophobic parts of these molecules are the hydrocarbon radicals of aliphatic alcohols or alkyl phenols.

In the Soviet Union, the properties of latices stabilized with non-ionogenic surfactants were first studied by Panich and Voyutsky as early as 1961. They found that the latices obtained with non-ionogenic surfactants, which are the products of copolymerization of mono- and dialkyl phenols containing sufficiently large amounts of ethylene oxide, are quite resistant to the action of electrolytes. Latices obtained with stabilizers which are more hydrophilic and contain a long hydroxyethylene chain are resistant to intensive stirring whereas a latex having a more hydrophobic stabilizer coagulates on stirring. Dilute latices with non-ionogenic emulsifiers have a small negative ζ-potential because extraneous ions present in a system are adsorbed by latex globules. The absolute value of the negative ζ-potential of latex globules having non-ionogenic stabilizers increases with pH. This means that hydroxyl ions are adsorbed and determine the charge.

Latices in the isoelectric state were obtained by introducing $AlCl_3$, and coagulation was not observed in them. Thus, their stability is caused not by electrostatic forces, but mainly by the hydration of the polar regions of stabilizer chains. However, the aggregative stability of latices containing a non-ionogenic stabilizer is lower in an isoelectric state than that of initial latices. Therefore, the charge of latex globules, which is caused by ion adsorption, contributes to the greater stability of latices.

The stabilizing action of hydration probably consists in ensuring effective repulsion when such hydrated layers interact (disjoining pressure).

Latent coagulation and gelation in latices stabilized by non-ionogenic surfactants occur only at elevated temperature under the action of electrolytes. The coagulation rate is the higher, the more intense are dehydrating factors: temperature, the concentration of an electrolyte, the type of a coagulating ion.

4. FOAMS

Typical foams are coarse, highly concentrated dispersions of a gas (usually air) in a liquid. The size of gas bubbles in such systems is about several millimetres and occasionally several centimetres. Owing to an excess of the gaseous phase and mutual compression, foam bubbles are not spheres, but polyhedron cells whose walls con-

sist of very thin films of a liquid dispersion medium. Foam films often exhibit interference, indicating that their thickness is commensurable with the wavelength of light.

Foam has a honeycomb structure because it consists of polyhedron cells. J. Plateau has established that, in conformity with the requirement of minimum free surface energy, three films always converge at one liquid edge of a cell, forming equal angles of 120° between them, and that only four edges can converge at a point. The large dimensions of gas bubbles and their compact arrangement in a foam preclude Brownian motion. Stable foams possess rigidity or mechanical strength due to their structure. In general, ordinary foams are very similar in structure to highly concentrated emulsions.

Gas/liquid (G/L) systems of low concentration where gas bubbles are away from one another should be distinguished from typical foams which are highly concentrated gas-in-liquid dispersions. Such dispersed systems are aerated water, beer, or sparkling wine which contain bubbles of carbon dioxide. These systems are more similar to dilute emulsions by their properties. However, because of the great difference in the densities of liquid and gaseous phases, such systems possess very low sedimentation stability and exist for a short time.

Foams are formed when a gas is dispersed in a liquid in the presence of stabilizers which in this case are known as *foaming agents.* Liquids without foaming agents do not produce a stable foam.

The strength and lifetime of foams depend on the properties of a film framework which are determined by the nature and concentration in a system of a foaming agent, adsorbed at the interface. Typical foaming agents in the case of aqueous foams are such surfactants as alcohols, fatty acids, soaps, soap-like substances, proteins, and saponin (glucoside which is extracted from plants). These substances determine also the stability of hydrocarbon-in-water emulsions.

Foam stability. Foam stability depends on the nature and concentration of a foaming agent. In the course of time, films between foam bubbles become thinner as a liquid runs off, the bubbles burst, foam is destroyed, and only a liquid phase, i.e., a solution of a foaming agent in water or some other liquid, remains.

Foam stability can be characterized by the lifetime of foam, i.e., by the time taken from the formation of foam to its complete destruction. This stability can be estimated also by passing air bubbles at a given rate, through a frothing liquid, and determining the equilibrium height of the foam column so formed. The equilibrium height of a foam column is established when the rate of foam destruction becomes equal to the rate of foam formation, and it is apparently a measure of foam stability. The stability can be also determined through the lifetime of a gas bubble at the interface between a liquid

and air. To this end, an air bubble is forced into a liquid by means of a capillary tube with a bent tip. The bubble floats up and, reaching the surface, remains there for a certain length of time before bursting. This lifetime of a bubble is usually proportional to the lifetime of a foam column as a whole.

When an air bubble is on the liquid surface, the film enveloping the bubble thins, as can sometimes be seen from a change in the interference colours of the film. When the thickness of the film is less than 0.01 μm, interference becomes almost unnoticeable, the film darkens since it reflects almost no light, and then it is destroyed. But foams can exist infinitely long when the liquid does not evaporate and there are no jolts or other external effects. For example, J. Dewar kept a soap bubble in existence for three years.

As B. Deryagin and A. Titiyevskaya found, a soap film which has reached the minimum thickness consists of two monolayers of molecules of a foaming agent that are separated by a polymolecular layer of water.

Since foam has a rather short lifetime and a liquid of a foam film always runs off before a foam bubble is destroyed, it follows that foam stability under ordinary conditions is of a kinetic nature whereas the role of a foaming agent consists mainly in retarding the run-off of a liquid.

Data given in Table 12.1 show that aqueous solutions of alcohols and fatty acids form slightly stable foams whose lifetime is below 20 seconds. The central members of the homologous series have the maximum lifetime of foam. The lower members of both series are apparently not surface-active enough to form stable foams, whereas the higher members of the series are not soluble enough.

Table 12.1. **Optimum Concentration of Aqueous Solutions of Foaming Agents and the Maximum Lifetime of Foams**

Foaming agent	Optimum concentration, mmol/l	Maximum lifetime of a foam, sec	Foaming agent	Optimum concentration, mmol/l	Maximum lifetime of a foam, sec
Alcohols			*Acids*		
Ethyl	280	5	Formic	450	4
Propyl	340	11	Acetic	200	8
Iso-butyl	90	12	Propionic	250	11
Iso-amyl	36	17	Butyric	1000	18
tert-Amyl	34	10	Valeric	15	9
Heptyl	0.7	8	Caproic	7.5	13
Octyl	0.3	5	Heptylic	1.5	16
			Caprylic	0.25	12
			Nonylic	0.07	5

Each alcohol or acid has an optimum concentration at which the foaming agent is the most effective. The most stable foams are usually formed at an average, rather low concentration of an alcohol or an acid. Fig. 12.9 gives an isotherm for the lifetime of foam as a function of the concentration of iso-amyl alcohol.

Soaps produce far stabler foams than alcohols and acids apparently owing to the presence of ionogenic groups in their molecules. Like for alcohols and acids, the maximum stability of foam relates to soaps having an average length of a hydrocarbon radical and to their solutions of average concentration.

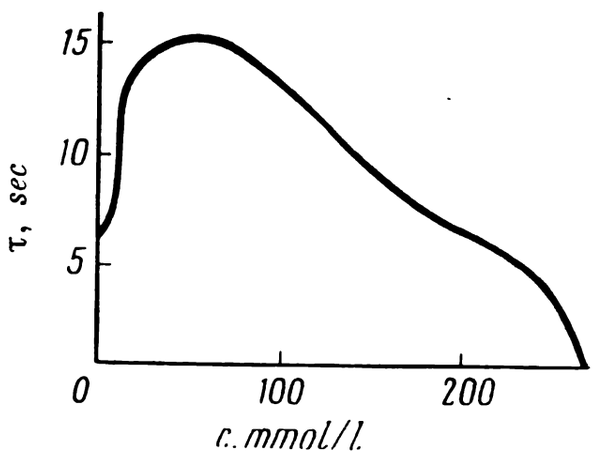

Fig. 12.9. Lifetime τ of foam as a function of the concentration c of iso-amyl alcohol

Foaming agents of high molecular weight behave differently. The lifetime of foams is very long in this case and can be hundreds and even thousands of seconds under ordinary conditions. The lifetime of foams is always the longer, the higher is the concentration of a foaming agent of high molecular weight.

Foam stability depends not only on the nature and concentration of a foaming agent, but also on temperature, the viscosity of a dispersion medium, the content of electrolytes in a liquid, and the pH of a medium. Unfortunately, there is not enough exact information on the effect of these factors on foam stability. An elevation of temperature is unfavourable for stability because a foaming agent is desorbed from the interface and the dispersion medium becomes less viscous, thus allowing a liquid in a film to run off more rapidly. Besides, an elevation of temperature accelerates the destruction of a foam also because the dispersion medium evaporates more rapidly and a film is dehydrated. Foams formed by foaming agents of low molecular weight become less stable when electrolytes which do not destroy foam are introduced into a liquid. Foams become more stable whenever the viscosity of a medium increases.

J. Perrin was the first to study "black" films. If a free film (or bubble) has been formed from a sufficiently concentrated solution of soap (e.g., sodium oleate), it gradually thins and changes interference colours. The film becomes white when a thickness of 1000 Å is attained. As the film thins further, less light is reflected, the film becomes grey, and its regions acquire different thickness. The uneven thinning of a film is a stepwise process. In the thinnest regions, the film is quite black.

P. Wells made several measurements of the thickness of soap films by interferometry and colorimetry; he has discovered that the thickness of a black film is several times less than that of the thinnest part of an ordinary film, and this fits in with Perrin's experiments. The minimum thickness of a black film is 42-45 Å, which is about the double length of a sodium oleate molecule.

Sheludko, Exerova, and Duyvis determined the thickness of a black film formed in surfactant solutions and confirmed the results of the previous investigations. They found that the thinnest film obtained with a solution of sodium oleate was 40 Å thick whereas films obtained with solutions of the wetting agents ОП-7 and ОП-20* were 85 Å and 100 Å thick, respectively (about the double length of a surfactant molecule). Such a small thickness is obtained only when the electrolytic concentration of a solution is sufficiently high. If the concentration is too low, thicker films are formed, and their equilibrium thickness gradually decreases as the concentration increases. This is in complete conformity with the DLVO theory.

Foam bubbles burst on standing as a result of which foam is destroyed. However, when foam is allowed to stand, bubbles not only burst but also small bubbles grow smaller, and large ones, larger. A. De Vries explains this phenomenon as follows. According to the laws of capillarity, the gas in small bubbles is under greater pressure than the gas in large bubbles. Pressure tends to become uniform by gas diffusion through a liquid film, and this reduces the dimensions of small bubbles and increases those of large ones. This phenomenon is similar to isothermal distillation when large droplets of a liquid grow at the expense of small ones because the liquid in the latter has greater vapour pressure. Such a tendency of foam is especially important when a foam film is very stable and foam is not destroyed in the ordinary way (e.g., foams obtained from a rubber latex).

As foam ages, its total volume diminishes. The reason for this becomes clear if the gaseous phase over foam is regarded as a single infinitely large bubble into which gas diffuses from foam bubbles. De Vries has found that the square of the radius of small bubbles diminishes linearly with time as foam ages. Such a conclusion fits in with the theory evolved on the basis of the above-mentioned concepts.

Causes of foam stability. Foam stability can be explained by various factors: (a) the Gibbs effect; (b) rather high surface viscosity or specific mechanical properties (structural-mechanical factor of stability) of a film; (3) the existence of hydrate or electric double layers in its near-surface layer which prevent the film from thinning (thermodynamic factor of stability). Let us consider these three factors.

* These are hydroxylated alkyl phenols with the number of hydroxyethylene chains being 7 or 20.

When foam is being obtained by passing air bubbles through a liquid or when the volume of foam diminishes slowly as a result of compression or destruction of its bubbles, foam films undergo local strains and therefore they must withstand both compression and extension. Low surface tension at the interface between a frothing liquid and air should promote the easy deformability of foam and its strength. But this is not so. Experiments have shown that the ability of a liquid film to change readily and rapidly the value of surface tension, rather than its low values, is important to foam stability. To withstand local deformation without rupture, a film must be able to increase surface tension upon local strains and decrease it upon local compressions. These changes compensate for local strains and the difference in stresses which originate in various regions of a film, and ensure its strength. Gibbs called this ability the *effective elasticity* of a film and interpreted it as follows. When a region of a film is extended, its surface increases and consequently the concentration of a surfactant at the interface decreases whereas surface tension in the expanded region increases. As a result, the region tends to compress more than all the adjacent non-expanded regions. An opposite phenomenon is observed when strain causes film compression.

Only films obtained from surfactant solutions can possess elasticity as Gibbs understood it. Films made out of individual liquids whose surface tension remains constant when films expand or compress have no such elasticity; therefore, stable foams cannot be obtained from such liquids. The stablest foams are usually produced from solutions of surfactants whose surface tension changes sharply with concentration, and not from those which possess minimum surface tension.

Account should be taken of the specific structure of real foam when explaining its stability from the standpoint of Gibbs. It is this structure that complicates the run-off of a liquid in foam films, and strongly affects the stability of the system. The framework of a foam consists of almost flat liquid films which are walls of cells. Bubble edges are formed in places where three films converge, and the surface of a liquid is very concave in them. According to the laws of capillarity, the pressure of a liquid is lower in these places, and therefore it is drawn from the plane parts of the foam framework into concave ones. As a result, a liquid flows to the edges in foam films, causing the films to thin spontaneously. But such flow can occur only within a film and not on its surface owing to the Gibbs effect. Indeed, if a liquid were to flow from the central part of a film to the edges, surface tension would increase in the central parts of the film; consequently, a liquid counterflow from the edges to the centre would immediately originate on the surface, and flow would thus stop. It follows that a liquid runs off as if the film surface were immo-

bile, i.e., the liquid flows, as it were, along a flat capillary. Apparently, a liquid runs off along such a capillary the slower, the thinner is a film.

The concepts considered above still cannot completely explain foam stability. First of all, it is difficult to understand the dependence of foam stability on the nature and concentration of a foaming agent from this viewpoint. When a liquid contains a sufficiently active foaming agent, the conditions of the flow of liquids in films should not depend on these two factors. But experiments have shown that this is not so. Secondly, a film should become more elastic as it thins when a liquid is drawn to the foam edges because the content of a surfactant in thin films is less and, consequently, its surface concentration will diminish more in extension. But if a film becomes more elastic as it thins, why does it burst?

This factor apparently determines stability of slightly stable foams which are stabilized with foaming agents of a low molecular weight.

Foams are highly stable when a very viscous or mechanically strong adsorption layer made of molecules of a foaming agent exists in films. Such an explanation was first proposed by J. Plateau in the last century, and then it was studied in more detail by Rehbinder. According to Rehbinder, highly viscous adsorption layers of gelatinous structure are formed on the surface of solutions of soaps or soap-like substances, and diffuse in the bulk of solution. The layers retard the flow of a liquid in a film, on the one hand, and impart high structural viscosity and mechanical strength to a foam film, on the other. But investigations carried out by A. Trapeznikov, A. Lawrence, and other workers have shown that stable foams appear also when there is no noticeable surface viscosity or when structural-mechanical properties are absent at the solution—air interface. K. Zotova and A. Trapeznikov explained the stability of foam films in a new way. They have found that surface-active colloidal components can pass over in a greater amount to a film than to an adsorption layer at the surface of a stock solution. This is due to specific conditions of film formation that promote continuous surface renovation and the exchange of surface-active components. A thixotropic structure may be formed in the bulk of a film between adsorption layers, greatly increasing the viscosity of this part of a film, when unstable colloidal aggregates originated in a solution pass into the film. The viscosity of the adsorption layers remains low in this case. Of course, the flow is greatly retarded and foams become more stable because of such a structure. The very long lifetime of foams stabilized with compounds of high molecular weight accords well with such an explanation of foam stability. In this case, there is almost no doubt that a highly viscous thixotropic structure is formed in the bulk of a film.

Let us now explain, using the thermodynamic factor of stability, why some foams are very stable.

Deryagin, who was the first to show the importance of this factor, proceeds from his concepts of disjoining pressure to explain the existence of foams. Disjoining pressure in the films of foam, stabilized with ionogenic substances, is caused by the repulsion of electric double layers which are formed by ions of a foaming agent in a solution near both surfaces of a film. Deryagin and Titiyevskaya proved the existence of such repulsion when they studied the compression of double-sided films, formed at the place of contact of two foam bubbles, by means of a precise method and a device which they made.

These investigations have shown that films obtained from aqueous solutions of sodium oleate, while thinning as a result of pressure, reached a certain constant thickness which did not change any more. The equilibrium thickness of such films was hundreds of angstroms when the content of electrolytes in a frothing liquid was low. Conversely, in sufficiently concentrated solutions of electrolytes, the equilibrium thickness of films was considerably less than the theoretically calculated one. This circumstance proved the electrostatic nature of disjoining pressure in this case. The thickness of the film did not depend on concentration at rather high concentrations of electrolytes (of the order of 0.1 N and more) when diffuse ionic layers are compressed to the utmost. However, the films remained stable because, under such conditions, repulsive forces of a non-electrostatic nature came into action, probably due to the hydration of the single layers of a foaming agent. Deryagin and Titiyevskaya have found that equilibrium thicknesses of adsorbed films of both ionogenic and non-ionogenic foaming agents do not depend on high concentrations of electrolytes and on temperature; therefore, these layers have a specific structure which confers on them properties of a special boundary phase.

The importance of hydration to foam stability was indicated by A. Trapeznikov and, even earlier, by D. Talmud. According to Trapeznikov, foams are stable when polar groups of molecules of a foaming agent are hydrated, and the flow of a liquid in a foam film slows down. The cohesion of the ends of hydrocarbon chains arranged at the interface facing the gaseous phase is required only for ensuring the integrity of the adsorption layer. The adsorption layer should be sufficiently mobile and, consequently, rarefied so that the ruptures formed when the liquid in the film flows would have time to "heal". Trapeznikov believes that foam destruction is caused by the dehydration of polar groups of the adsorption layer when the dispersion medium is continuously drawn off. Consequently, two- and then three-dimensional aggregates of molecules of a foaming agent appear; they do not have stabilizing action and a film ultimately ruptures.

Thus, there are several factors which explain foam stability. At present, many workers hold that there is no single theory of foam stability: the existence of foams depends on foaming agents and the conditions under which foams are obtained.

Methods of obtaining and breaking foams. Practical importance of foams. Foams are obtained by passing bubbles of a gas (usually air) through a solution of a foaming agent or by intensively stirring the solution. Gas bubbles in a liquid become surrounded with an adsorption layer of a foaming agent, rise to the surface, approach the adsorption layer on it, stretch it, and thus form double-sided films. If these films are sufficiently strong, the bubbles form foam.

The role which the nature of a stabilizer plays in foam formation was dealt with in the preceding section of this chapter.

It is often necessary to destroy the foam or take measures to preclude its formation. To this end, substances which, while possessing high surface activity, do not produce stable foam are introduced into a system. They force out a foaming agent from a liquid surface and thus make it impossible for foam to exist. Various substances, such as alcohols and esters, are used as antifoaming agents. Cyclohexanol, amyl and octyl alcohols, and mixtures of higher alcohols obtained as by-products in the synthesis of methanol, are among the alcohols used most commonly for breaking foams. Another method of destroying foam is by "burning" a foam film by high temperature. Various mechanical treatment can also be used to break stable foams..

Foam formation and foams are of great practical importance. The role played by foam in flotation has already been mentioned in Chap. 6, Sec. 5. Foam formation is a favourable factor in laundering. Surface-active impurities which pass into foam can be removed from some liquids by making and then removing foam. This technique can be used to extract valuable surfactants from a solution. Foams are important to fire fighting. Since foams used to this end contain carbon dioxide as a dispersed phase, they do not allow air to reach burning objects when deposited on them and thus help to put out fire.

Sometimes, foam formation may be unfavourable. For example, it is difficult to stir some solutions when foam is readily formed. The formation of abundant foam hinders the evaporation of solutions in evaporators and causes the loss of a valuable liquid when foam is thrown over. In such cases, the above-mentioned antifoaming agents are used.

5. SYSTEMS HAVING A SOLID DISPERSION MEDIUM

Colloidal systems having a solid dispersion medium or, as they are often called, *solid sols*, though being of great practical importance, so far did not attract much attention in colloid chemistry because they have unusual properties in comparison with those of other colloidal systems. Of course, systems having a solid dispersion medium do not possess molecular-kinetic properties and aggregative stability which are important to other colloidal systems. Let us consider some of these systems and their characteristics.

Colloidal and microheterogeneous systems having a solid dispersion medium can be divided, like lyosols, into systems having gaseous, liquid, and solid dispersed phases.

Systems having a solid dispersion medium and a gaseous dispersed phase, G/S, are often called *solid foams*. These foams, like liquid foams, are usually related to microheterogeneous or even coarsely dispersed systems owing to the large dimensions of bubbles of the gaseous phase. An example of natural solid foam is pumice, a porous, very light rock of vulcanic origin which is used as an abrasive for polishing and grinding, and for making pumice concrete. Among artificial solid foams are foam glass and cellular foam concrete which are widely used as building materials and insulators. The advantages of these materials are low density, low thermal conductivity and rather high strength owing to their cellular structure and to the strength of the dispersion medium. They include artificial porous polymer-based materials (microporous rubber, plastic foams).

Systems having a solid dispersion medium and a liquid dispersed phase, L/S, which by analogy can be regarded as *solid emulsions*, are encountered rather rarely. An example of such systems is so-called black phosphorus which is obtained by dispersing metallic mercury in molten phosphorus.

Systems having a solid dispersion medium and a solid dispersed phase, S/S, are of the greatest importance. This class of colloidal and microheterogeneous systems includes coloured precious and semi-precious stones, coloured glass, enamel, minerals, and alloys.

At the beginning of this textbook, we have seen that precious and semi-precious stones are, as a rule, alumina or quartz in which oxides of various metals are dispersed. Coloured glass is usually ordinary silica glass which contains traces of impurities of a colloidally dispersed substance that imparts colour to glass. For example, ruby glass contains highly dispersed gold as a dispersed phase. The content of gold in ruby glass varies from 0.01 per cent (pink glass) to 0.1 per cent (bright red glass) whereas the dimensions of particles are 4-30 nm, and rarely more than 150 nm. Less expensive glass having the same ruby colour can be obtained by dispersing such me-

tals as silver, selenium, and copper instead of gold. Glass of different colour can be obtained when it is alloyed with other substances.

Enamel, a glassy opaque substance, is deposited in a molten state on metallic or ceramic surfaces so as to either make them beautiful or impart greater stability to chemical action. Enamel is also silica glass containing particles of pigments which make it opaque and coloured. Oxides and salts, e.g., SiO_2, TiO_2, and calcium phosphate, can be used as such pigments.

Glass obtained by alloying metal oxides with borax is similar to coloured silica glass. In analytical chemistry the colour of such glass ("beads") indicates the chemical nature of a substance alloyed with borax.

Blue rock salt, a representative of colloidal systems in nature, is blue because colloidally dispersed metallic sodium is present in traces (0.0001 per cent) in sodium chloride crystals. As early as 1905, H. Siedentopf synthesized blue rock salt by heating sodium chloride crystals in sodium vapours. The salt first turned yellow which corresponded to high dispersity of sodium particles. However, on further alternating heatings and coolings, sodium particles gradually aggregated and crystals became blue. Experiments carried out later have shown that blue salt can be synthesized also when sodium chloride crystals are exposed to X-rays and radioactive radiation.

The presence of particles of metallic sodium in blue rock salt is confirmed by the fact that the dissolution of such a salt in water is accompanied with a noticeable evolution of hydrogen from water being decomposed by sodium. In nature, sodium ions are reduced in rock salt to metal by gaining electrons upon β-irradiation. The source of radioactive radiation can be the radioactive isotope of potassium, ^{40}K, which is always present in traces in natural rock salt. Calculations have shown that the content of ^{40}K in rock salt is quite enough to cause the appearance of blue colour in the course of geological periods.

S/S systems include also rocks. Many vulcanic rocks have a colloidal or microheterogeneous structure because, as magma cools, its components crystalize and thus constitute a dispersed phase. Sedimentary rocks have a colloidal structure because they are formed when very fine particles of silica, clayey minerals, humus substances, ferric hydroxide, and shells of the *Diatomaceae* algae settle in inland waters or seas. Rocks are material out of which aerosols and lyosols are formed in nature as a result of weathering and erosion.*

Other S/S systems are heterogeneous alloys which include most metals used in technological processes. An alloy can have a structure

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* Much information on the colloidal structure of rocks and on the role of colloidal processes in the formation of the Earth's crust is found in F. Chukhrov's book *Kolloidy v zemnoi kore* (Colloids in the Earth's Crust), Izd. Akad. Nauk SSSR, Moscow, 1955.

of a molecular solution, a colloidal system, or a coarsely dispersed system, depending on the conditions under which it is obtained. In steel, for example, we encounter all the transitions from a true solution (austenite) through a colloidal solution (martensite) to a microheterogeneous system (pearlite). In cast iron, the dispersed phase is carbon particles whose dimensions approximate colloidal ones.

Among typical colloidal properties of systems having a solid dispersion medium, the ability to scatter light is expressed best of all. As we have seen at the beginning of the textbook, the term "opalescence" is derived from the opal mineral whose ability to scatter light is very pronounced. Siedentopf and Zsigmondy made their first ultramicroscopic observations with ruby glass. Of course, light scattering by systems having a solid dispersion medium can be observed only when the medium is transparent.

Ordinary coagulation cannot occur in systems having a solid dispersion medium owing to its enormous viscosity which prevents particles from colliding with one another. But particles in such systems can grow coarser as a result of the isothermal distillation of the substance of a dispersed phase. Such coarsening occurs, for example, if ruby glass is heated for a long time at a temperature when metal vapour pressure is sufficiently high. At very high temperature when the dispersion medium melts, true coagulation can also be observed in such systems and their colour changes if the medium is transparent. For example, at high temperature, ruby glass changes from red to violet and then to dark blue as particles aggregate. Stannic oxide, present in glass, has a protective effect and prevents aggregation.

Colloidal and microheterogeneous systems having a solid dispersion medium are usually formed by condensation from a melt. When a melt, being a homogeneous system, cools, a dispersed phase is formed and its particles remain distributed in the solidified system. That is how rocks having a colloidal or a microheterogeneous structure are formed when magma cools. Plastic foams are produced industrially somewhat differently. A blowing agent is introduced into a polymer and it evolves gas on heating or under some other action. Gas may remain in a polymer as minute closed bubbles or may form open winding pores in it.

A gas, a liquid, or a solid is dispersed in a molten medium when colloidal or microheterogeneous systems having a solid dispersion medium are obtained. Such a melt, which still possesses liquid properties, is known as a *pyrosol*. When a pyrosol cools, it solidifies and forms a colloidal or a microheterogeneous system having a solid dispersion medium. As we have seen from the example of ruby glass, pyrosol stability and, consequently, the dispersity of a system having a solid medium can be increased by introducing an appropriate stabilizer.

13

COLLOIDAL SURFACTANTS *

Most colloidal solutions are heterogeneous and thermodynamically non-equilibrium systems. But there are systems which are true solutions under some conditions, and sols, cross-linked liquids, or even gels, under others. Such systems are reversible and are in thermodynamic equilibrium:

$$\text{true solution} \rightleftarrows \text{sol} \rightleftarrows \text{gel}$$

For a conversion to be made from one state to another, it is enough to change the concentration of a solution, temperature, and pH, or to introduce an electrolyte into a system. By changing the conditions under which a system exists, we can obtain either true (homogeneous) solutions with molecular dispersity or heterogeneous systems whose particles are aggregates made out of many molecules. Such particles, like electroneutral particles in lyophobic colloidal systems, are called micelles. But, unlike the micelles of colloidal systems, they are thermodynamically stable and do not change until the equilibrium of a system shifts under the action of external factors. The stability of micelles is characterized by the dissociation rate, i.e., the mean time of residence of a molecule in a micelle.

The systems in which such reversible transitions occur include aqueous solutions of many surfactants, i.e., soap and soap-like substances, and also solutions of tannins (tanning agents) and some dyes. If these solutions contain particles consisting of a large number of molecules, they can be related to lyophilic colloidal systems because they possess properties of colloidal systems, i.e., heterogeneity and high dispersity, but unlike lyophobic colloidal systems, they are in thermodynamic equilibrium and aggregatively stable.

Substances producing such solutions were formerly called semi-colloids. But this term is not accurate. Therefore, it is better to use

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* This chapter was written in collaboration with R. Panich.

the term "surfactants" for surface-active substances which are capable of making a transition from a state of molecular disintegration to a colloidal state.

Since soaps are the most typical colloidal surfactants and are widely used in the national economy, properties of colloidal surfactants will be considered in this chapter mainly by taking the example of soaps.

1. PRINCIPAL CONCEPTS AND CLASSIFICATION OF COLLOIDAL SURFACTANTS

Colloidal surfactants, like all surfactants, are characterized by low true solubility and the ability to reduce surface and interfacial tensions in dilute solutions as a result of the adsorption and orientation of molecules at the interface. But at a certain concentration, known as the *critical concentration of micelle formation* (CCMF), molecular aggregates, or micelles, are formed in a solution; as a result, total surfactant solubility, caused by the formation of a colloidal solution together with a true one, sharply increases while molecular solubility remains unchanged and equal to CCMF.

For a surfactant to be capable of forming micelles, it must meet two requirements: it must have a sufficiently large hydrocarbon radical which reduces solubility in water, on the one hand, and must have a sufficiently active polar group which promotes its solubility, on the other. Not all surfactants meet these requirements. For example, micelle formation is not characteristic at all of the homologous series of aliphatic alcohols. When compounds have less than seven carbon atoms, micelle formation is hindered by the small length of a hydrocarbon radical; when higher homologues are concerned, the process is hindered by the rather poor hydrophilic nature of a polar group. Moreover, for many colloidal surfactants, e.g., hydroxyethylated alcohols, micelle formation is possible only when a hydrocarbon radical has over 7-8 carbon atoms, regardless of the number of hydroxyethyl groups, that is, the polarity of the hydrophilic moiety of a molecule.

The surface tension isotherm, which characterizes the dependence of this quantity on the concentration of a colloidal surfactant in a solution, consists of an almost rectilinear segment for the drop in surface tension, a curvilinear segment described by Shishkovsky's equation, and an almost horizontal segment in the range of concentrations higher than CCMF. On this last segment, surface tension almost ceases to change because the newly introduced surfactant molecules are not adsorbed at the solution—air interface, but form micelles in a solution. For surfactants which do not possess colloidal solubility, the horizontal segment of the surface tension isotherm is shifted to the range of higher concentrations.

According to the structure of the molecules of colloidal surfactants, they are subdivided into three main groups: anionic, cationic, and non-ionogenic ones.

Anionic surfactants. These surfactants dissociate in water, forming negatively charged surface-active ions. Anions are adsorbed by the surface from solutions of such surfactants as a result of which it becomes negatively charged. The most important representatives of this group of colloidal surfactants are ordinary soaps and sulphonates.

Ordinary soaps are salts of saturated and some unsaturated carboxylic acids. Colloidal properties are exhibited only by the salts of

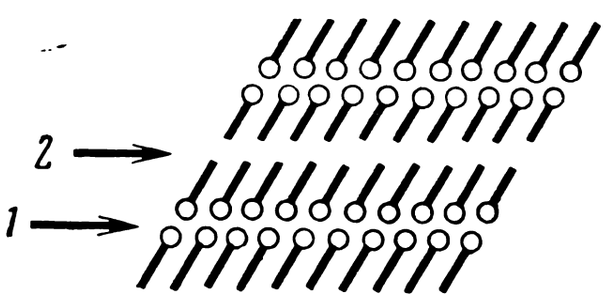


Fig. 13.1. Schematic structure of the sodium oleate crystal:
1—plane which corresponds to the —COONa groups; *2*—plane which corresponds to the —CH_3 groups

fatty acids that have at least 10 and not more than 22 carbon atoms in a hydrocarbon chain. As we have seen in Chap. 5, salts of fatty acids of low molecular weight are too water-soluble to exhibit these properties noticeably. Salts of fatty acids that have more than 22 carbon atoms in a chain almost do not dissolve in water.

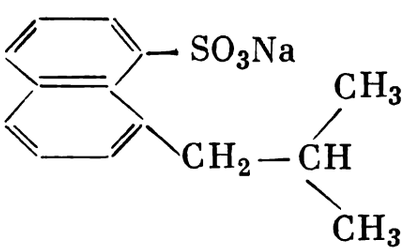
Sodium soaps of palmitic, stearic and unsaturated oleic acids, obtained in large amounts from animal fat, are widely used in technological processes: sodium palmitate, $C_{15}H_{31}COONa$; sodium stearate, $C_{17}H_{35}COONa$, and sodium oleate, $C_{17}H_{33}COONa$. Potassium and ammonium soaps of these acids, being in a liquid state under ordinary conditions, are of less importance.

Soaps having di- and trivalent cations, e.g. calcium, magnesium, and aluminium, are water-insoluble, but they form colloidal systems in hydrocarbon media. They are used in mineral grease and as stabilizers of second-order (w/o) emulsions.

Ordinary commercial soaps contain a large amount of water and often impurities of various substances, especially electrolytes, and this must be taken into account when they are used. Pure soaps can be isolated from solutions in crystalline state. X-ray analysis has shown that soap crystals have a laminar structure, and molecules in bimolecular layers face one another by their non-polar, i.e., hydrocarbon ends (see Fig. 13.1). In this case, molecules are usually arranged at an angle to the plane in which polar groups lie.

Detergency is possessed not only by the salts of fatty acids, but also by the salts of naphthenic acids which are alicyclic compounds. These salts are contained in naphtha soap which is obtained when kerosene and solar oil are refined.

Colloidal surfactants containing a sulpho group as an active group are the salts of sulphonic acids having high molecular weight and a general structure $C_nH_{2n+1}SO_3M$ for alkyl sulphonates or $C_nH_{2n+1}C_6H_4SO_3M$ for alkyl aryl sulphonates (M stands for a monovalent cation of sodium, potassium, or ammonium). This group includes also the salts of alkyl-substituted naphthalene sulphonic acids, e.g., the sodium salt of *iso*-butyl naphthalene sulphonic acid



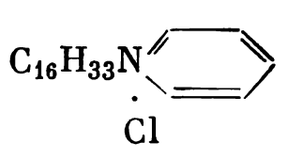
Compounds of this type are known as Nekals in technology.

Alkyl sulphates, i.e., sulphoesters of higher alcohols and their salts $C_nH_{2n+1}—O—SO_3M$, are now widely used as surfactants.

Since sulphonic acids are strong acids, not only their salts with monovalent cations, but also those with polyvalent cations and sulphonic acids themselves are sufficiently water-soluble and produce aqueous solutions having all the characteristics of "soap" solutions. This is an important advantage of sulpho soaps over ordinary ones because they can be used in hard water and even in an acid medium.

Cationic surfactants. When these surfactants dissociate in water, they yield positively charged surface-active ions. Cations are adsorbed by the surface from the solutions of such surfactants as a result of which it becomes positively charged. This is often of practical interest. For example, positively charged particles of a dispersed phase, which are stabilized by such surfactants, are selectively adsorbed (bound) from an impregnating bath by a negatively charged plant fibre much more intensively and thoroughly than negatively charged particles stabilized by anionic surfactants.

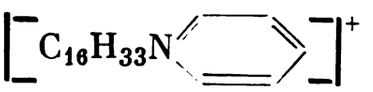
Examples of cationic surfactants are octadecyl ammonium chloride, $C_{18}H_{37}NH_3Cl$, tetrabasic ammonium salts such as cetyl trimethyl ammonium chloride, $C_{16}H_{33}(CH_3)_3NCl$, and pyridine compounds which are substituted at the nitrogen atom, e.g., cetyl pyridinium chloride



All these substances dissociate in water into chloride anions and the following cations:

$$[C_{18}H_{37}NH_3]^+$$

$$[C_{16}H_{33}(CH_3)N_3]^+$$



Anionic and cationic surfactants usually cannot coexist in an aqueous solution because a poorly dissociating salt of a high molecular weight and insoluble in water is formed from a large cation and a large anion in such a solution.

Non-ionogenic surfactants. This group includes substances whose molecules are incapable of undergoing dissociation. Diphilic molecules of such surfactants consist of a long hydrocarbon chain having several polar, but non-ionogenic, groups at the end which make these substances soluble. Such groups are hydroxyl or ether ones.

An example of non-ionogenic surfactants is compounds obtained when a molecule of an alcohol having high molecular weight (or some other organic compound, such as an acid or a phenol) reacts with several molecules of ethylene oxide:

$$C_nH_{2n+1}OH + m\underset{\diagdown\,O\,\diagup}{CH_2-CH_2} \longrightarrow C_nH_{2n+1}(OCH_2CH_2)_mOH$$

Non-ionogenic surfactant molecules are schematically denoted in the following way:

hydrocarbon radical hydroxyethylene chain

The hydroxyethylene chain is somewhat hydrophilic owing to the interaction between the ether oxygen atom and water molecules. Apart from the hydration water, the hydroxyethylene chain, which is sufficiently long and forms coils in a solution, binds water also owing to the entropy effect. Therefore, addition products acquire water-solubility, beginning with a definite number of hydroxyethylene groups that depends on the molecular weight and structure of the hydrophobic part of a molecule.

A substantial advantage of hydroxyethylated surfactants is that their hydrophilic nature can be controlled in synthesis by changing not only the number of carbon atoms in a hydrophobic chain, but also the number of hydroxyethylene groups. As a result, substances having preset properties intended for a specific field can be obtained. Another specific feature of these substances is that they do not form

salts and are therefore well soluble in hard water. In addition, non-ionogenic surfactants can be used together with ionogenic ones. Hydrophobic surfaces become hydrophilic when non-ionogenic surfactants are adsorbed from aqueous solutions.

We dealt here only with the typical representatives of colloidal surfactants and soap-like substances. In the last 40-50 years, chemistry and technology of surfactant production have developed very rapidly, and now hundreds of synthetic surfactants are known.

An important characteristic of colloidal surfactant molecules, which determines their surface and volume properties and consequently their utilization, is the ratio between hydrophilic and hydrophobic (lipophilic) groups of molecules, known as the *hydrophile-lipophile balance* (HLB). At present, there is no strict theory that makes it possible to determine the value of HLB from either the molecular structure or the physico-chemical properties of a substance. As a first approximation, use is made of the semi-empirical HLB system which was elaborated by Griffin and Davis. This system makes it possible to quantitatively estimate from the energy standpoint, in the form of nominal group numbers, the degree of interaction between water and individual groups constituting a surfactant molecule. The group numbers of hydrophilic groups are positive, and those of lipophilic ones, negative.

The HLB numbers of various surfactants can be calculated by special formulas as the sum of group numbers, or they can be determined experimentally. The more the balance is of a hydrophilic nature, the higher is the HLB number. The HLB number of non-ionogenic surfactants is usually not higher than 20; for ionogenic surfactants, e.g., potassium oleate, it is 20, and for potassium lauryl sulphate, it is about 40. The HLB numbers determine the regions of surfactant application. For w/o emulsions, the HLB value should change within the range of 3-6; for wetting agents, it is equal to 7-9; for detergents, it is usually within the range of 13-15; for o/w emulsions, it ranges from 8 to 18, depending on the nature of an oil.

The HLB system is formal to a certain extent because it is based on the stoichiometric composition of a compound and does not take account of the geometry of its molecular structure, such as isomerism. It makes it possible to determine the regions of surfactant application without characterizing its effectiveness well enough.

2. STATE OF SURFACTANTS IN A SOLUTION

True surfactant solutions. The greatest possible concentration at which colloidal surfactants are still in an aqueous solution in molecular (ionic) form, i.e., the critical concentration of micelle forma-

tion, is not high: it changes within the range of 10^{-5}-10^{-3} mol/l. Soaps, which are weak electrolytes, can exist in a solution not only as ions ($RCOO^-$, M^+), but also as undissociated molecules (RCOOM) and the products of their hydrolysis, i.e., molecules of fatty acids (RCOOH). Salts of strong acids, e.g., sulphonic acids, are in the form of ions in a solution whereas non-ionogenic surfactants are in the form of undissociated molecules.

Causes of micelle formation. Molecules begin to aggregate and micelles are formed above the critical concentration of micelle formation of surfactants in aqueous solutions.

The state of a solution in the case of micelle formation can be regarded as a reversible equilibrium which obeys the law of mass action. For the simplest case of undissociated molecules, e.g., non-ionogenic surfactant molecules, the equilibrium can be described by the equation

$$mx \rightleftarrows (x)_m$$

Another approach to this phenomenon is based on the assumption that micelle formation consists in the origination of a new phase in the water—surfactant system. In this case, micelles are regarded as a sort of phase with limiting dispersity (pseudo-phase) because, unlike true phase separation, micelle formation does not lead to an infinitely large number of molecules in an aggregate (the number of molecules in an aggregate is called the aggregation number). The phase theory of micelle formation, which most scientists accept, is confirmed by at least two circumstances: (1) the constancy of concentration of a molecularly dissolved surfactant when its total concentration is higher than CCMF, and (2) the presence of an abrupt discontinuity in the CCMF region on the curves for the physico-chemical properties plotted as a function of concentration. A thermodynamic examination shows that both approaches are justified when aggregation numbers are large (25 and more).

An aggregate of surfactant molecules is formed from hydrocarbon chains, and the hydrophilic parts of molecules are arranged on the outer surface of a micelle. Aggregates of hydrocarbon chains appear in aqueous solutions under the action of cohesive forces between water molecules which are greater than the forces of mutual attraction of water molecules and hydrocarbon chains. Water molecules "force out", as it were, hydrocarbon chains from a solution, and this is accompanied by a decrease in the enthalpy of a system. Micelle formation is hindered by the forces of mutual repulsion acting between the hydrophilic parts of surfactant molecules. For ionic surfactants, this repulsion is caused by the electrostatic interaction between ionogenic groups bearing a charge of the same sign, and for non-ionogenic surfactants, by osmotic forces which originate as a

result of the rise in the concentration of hydroxyethylene chains in the peripheral part of a micelle. Moreover, micelle formation is hindered by a decrease in entropy owing to the better ordering of a system on aggregation. A growth in the energy of repulsion of polar groups and a decrease in entropy compensate for the loss of energy of a system when hydrocarbon chains aggregate, and lead to the establishment of equilibrium values of CCMF and the micelle dimensions.

According to these traditional concepts, a decrease in the free energy of a system in micelle formation is caused by a diminution in the enthalpy of the system, and, consequently, micelle formation should be accompanied by heat evolution. But the heats of micelle formation determined experimentally were found to be small and, in some cases, even to have a negative value. Therefore, micelle formation was accompanied by heat absorption, apparently, owing to the specific properties of water that are caused by the existence of structures of a short-range order in water.

Various models of the state of water have been proposed. They all presume the formation of an ice-like tetrahedron structure in which water molecules are bound to one another with hydrogen bonds. In such a structure, every water molecule is surrounded, on the average, by four other water molecules. The tetrahedron structure of water was first predicted in the classical work by J. Bernal and R. Fowler, and was confirmed later by X-ray diffraction investigations. Apart from the molecules which are in the skeleton, there are free water molecules which are not bound by hydrogen bonds. These molecules partially fill the loose packing regions within the water structure and move in them. Constant heat exchange occurs between skeleton molecules and free ones as a result of thermal motion. A drop in temperature causes a diminution in the number of free molecules, i.e., it strengthens, or stabilizes, the water structure. An elevation of temperature produces an opposite effect: the number of molecules in a skeleton decreases and the tetrahedron structure of water weakens.

Loose packing regions in the ice-like structure of water can be regarded as voids which are important in the dissolution of non-polar organic substances in water. In dissolution, the molecules of these substances penetrate into the water structure, and this stabilizes the structure and reduces the internal energy of a system. One of the possible explanations of this phenomenon, proposed by O. Samoilov, is that the molecules of non-polar organic substances, while filling voids, hinder the movement of free water molecules and their heat exchange with the skeleton molecules. This promotes the stabilization of the water structure. Since surfactants contain a non-polar hydrocarbon chain, their dissolution also stabilizes the water structure.

The hydrocarbon parts of surfactant molecules associate in an aqueous medium simultaneously with surfactant dissolution, and this is known as *hydrophobic interaction*. This interaction is caused when the water structure weakens as hydrocarbon chains pass over from aqueous surfactant solutions to the micelle nucleus where van der Waals bonds originate between them. The entropy of a system becomes greater due to the destruction of the water structure and an increase in the conformation entropy of hydrocarbon chains in a

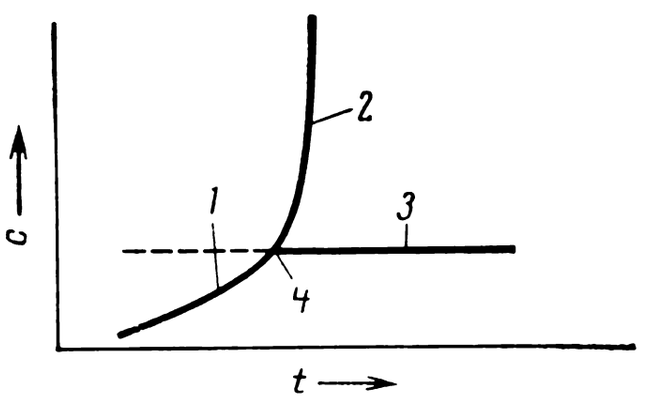


Fig. 13.2. Phase diagram of surfactant solutions near the Kraft point (c—surfactant concentration in a solution; t—temperature):
1—curve for the molecular solubility of surfactants below the Kraft point; *2*—curve for solubility (molecular or micellar) above the Kraft point; *3*—curve for molecular solubility (CCMF) above the Kraft point; *4*—Kraft point

micelle nucleus, in comparison with their entropy in an aqueous phase. It has been shown in the works by P. Rehbinder and Z. Markina, that micelle formation is a typical case of hydrophobic interaction. This means that a new constituent, an increase in the entropy of a system, appears in the energy balance of micelle formation, determining the entropy nature of micelle formation in many cases. Of course, an opposite process, a drop in entropy, also occurs in micelle formation. As a result, small micelles appear as a compromise, as it were, since entropy would decrease to a considerable extent in the formation of large micelles.

Micellar solutions of ionic surfactants can be formed only above a certain critical temperature, the *Kraft point* (Fig. 13.2). At low temperature, a hydrated solid surfactant forms a swollen gel which is in equilibrium with the true solution (segment *1*). At the Kraft point, the hydrocarbon chains of surfactants pass, as it were, into a liquid state. In this case, the oriented layers of surfactant molecules in a gel disintegrate into particles of colloidal dimensions, i.e., micelles, as a result of the thermal motion of hydrocarbon chains. The formation of micelles from a gel is accompanied by an increase in entropy which promotes this process. The total solubility of surfactants sharply grows (segment *2*) while true solubility, characterized by the critical concentration of micelle formation, does not

change considerably (segment *3*). The Kraft point lies below the melting point of a solid surfactant because the surfactant is hydrated in a swollen gel and this facilitates melting. Micelles can be regarded as a liquid phase since they are formed only above the Kraft point. It is evident that the hydrocarbon nucleus of micelles is in a liquid state also from the fact that they can form mixed micelles with various additives. Most hydrated non-ionogenic surfactants are in a liquid state at a sufficiently low temperature, and therefore the Kraft point does not exist for them.

Micelle structure. At a critical concentration of micelle formation in a system, *Hartley micelles* are formed from individual surfactant molecules. These micelles are spherical aggregates in which the hydrocarbon chains of a molecule are interwoven while polar groups are turned outwards (into water). The number of surfactant molecules in such an aggregate is usually within the range of 50-100, but it can reach even 1000. According to G. Hartley, the diameter of such a spherical aggregate is approximately double the length of a surfactant molecule out of which it is made.

It is not difficult to see that, for ionogenic surfactants, the structure of such a spherical aggregate completely coincides with that of a typical colloidal micelle. Indeed, aggregated hydrocarbon chains, which constitute, as it were, a drop of liquid hydrocarbon, act in a micelle as an aggregate of an ordinary micelle while the partially dissociated ionogenic groups in water form an electric double layer.

Micelles of a different structure are formed at higher surfactant concentrations in solutions. As the concentration of a solution grows, micelles become larger and hydrocarbon chains are arranged increasingly parallel to one another in them. As a result, plate-like micelles are formed; they consist of two layers of surfactant molecules which face each other by their hydrocarbon chains whereas their ionogenic groups are turned outwards. These micelles are structurally similar to a two-dimensional crystal and can have infinitely large dimensions in two directions. Plate-like micelles of ionogenic surfactants bear a weaker charge than spherical ones because the dissociation of ionogenic groups decreases at a rather high surfactant concentration when plate-like micelles are formed. Therefore, plate-like micelles are arranged parallel to one another, and the adjacent micelles face each other with their surfaces which contain hydrated groups of surfactant molecules. Owing to the formation of plate-like micelles and their characteristic arrangement, sufficiently concentrated solutions can convert into a gel which has a peculiar structure of bands and films visible under a microscope.

J. McBain was the first to assume that plate-like micelles existed in sufficiently concentrated soap solutions, and therefore they are

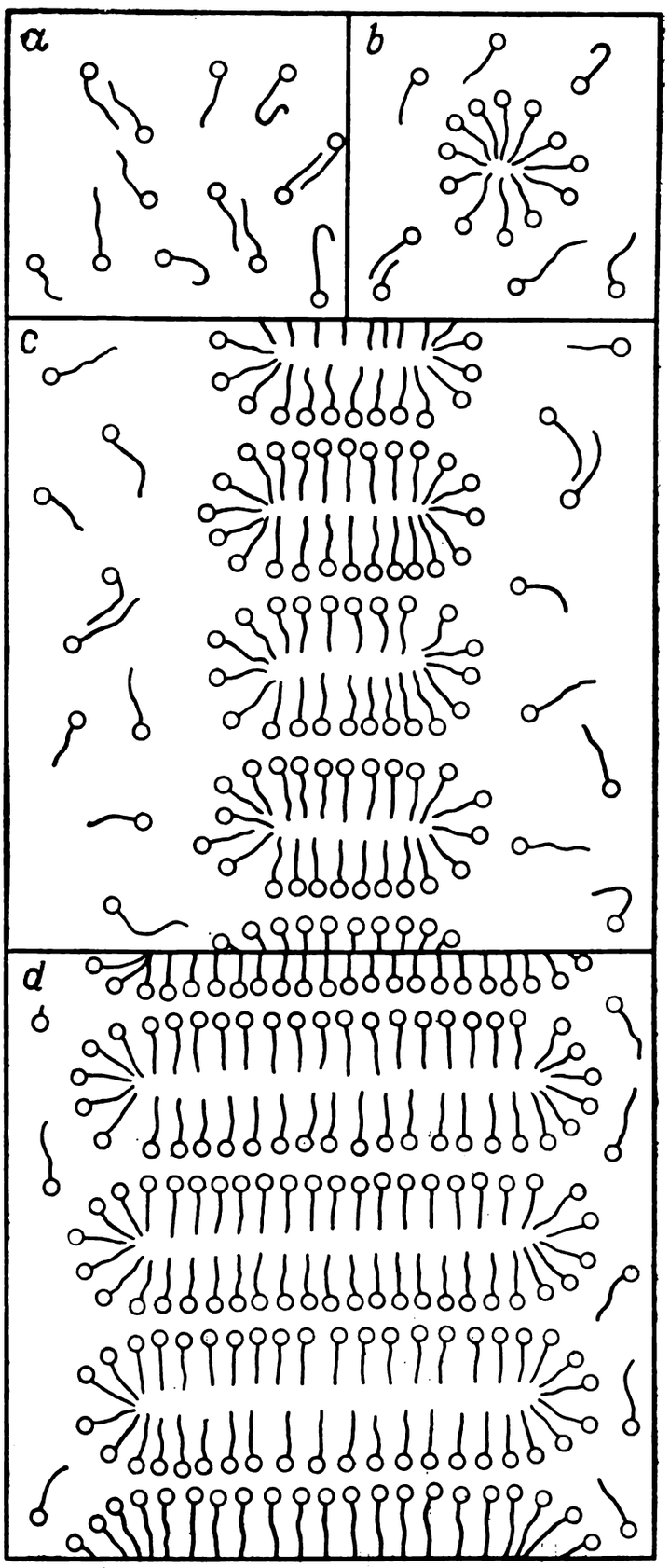


Fig. 13.3. Scheme of the formation of micelles in soap solutions:
a—diluted solution containing individual soap molecules and ions; *b*—a more concentrated solution containing spherical micelles; c, *d*—concentrated solutions containing plate-like micelles

often called *McBain micelles*. The existence of plate-like micelles of soap was later proven by X-ray analysis.

Fig. 13.3 schematically shows the formation of micelles in surfactant solutions as their concentration grows.

The determination of critical concentration of micelle formation. The methods are based on the fact that, when micelles are formed, all the properties of a surfactant solution change, and the change is the more sudden, the higher is the number of aggregation of molecules. It has been established nephelometrically that micelle formation causes a sharp increase in light scattering by a surfactant solution because it becomes heterogeneous.

McBain has shown that the concentration dependence of the osmotic coefficient* for soap solutions is schematically expressed by a curve in Fig. 13.4. The curve, unlike a monotonic one that is typical of weak electrolytes which do not form micelles, consists of three segments which correspond to (1) the pre-critical region, (2) a region in which the osmotic coefficient sharply changes with concentration, and (3) a post-critical region where the curve is almost parallel to the concentration axis. The shape of the first segment of the curve changes at a point which corresponds to a diminution in the osmotic activity of a solution as a result of the formation of spherical micelles, i.e., at a point which corresponds to CCMF.

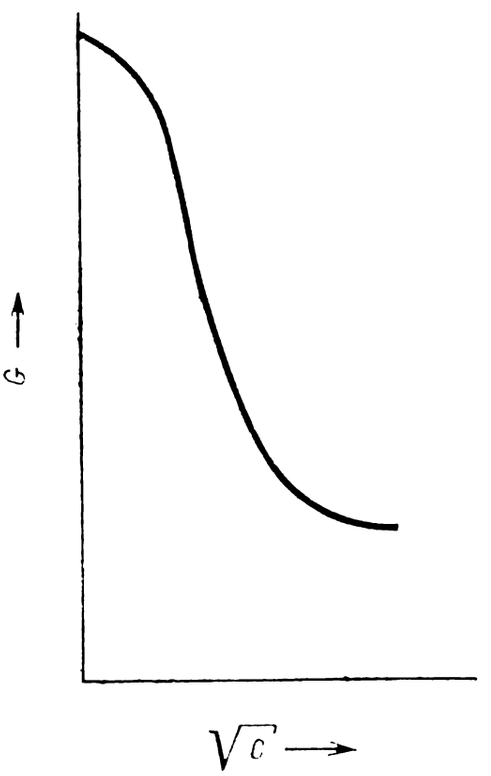


Fig. 13.4. Dependence of the osmotic coefficient G on the concentration c of a soap solution

The equivalent electric conductivity of a surfactant solution changes with concentration similarly to this curve. Fig. 13.5 shows typical concentration curves of equivalent electric conductivity for solutions of ordinary soaps. The initial curve segments, which correspond to the pre-critical region, are not plotted on the graph because of its small scale. However, we can see from the shape of the second and third segments that the equivalent electric conductivity of soap solutions containing 12 or more carbon atoms in a chain sharply drops in the region of low concentrations. Then, it reaches a minimum at a point, which corresponds to micelle formation, and later it somewhat increases again. In this case, as the molecular weight of surfactants increases, the minimum shifts towards lower concentrations and becomes more pronounced. According to Hartley, a

* Bjerrum's osmotic coefficient is equal to the ratio of the actual number of particles in a solution to that which would have existed if an electrolyte was completely dissociated.

drop in equivalent electric conductivity with an increase in the soap concentration of a solution is caused by the partial binding of counterions by ionized micelles. This binding occurs under the action of considerably strong electric forces which are due to ionic micelles formed in a system and bearing a high charge. It is not quite clear why equivalent electric conductivity increases after reaching the minimum.

Lastly, CCMF can be determined by a change in the surface tension of a colloidal surfactant solution when its concentration increas-

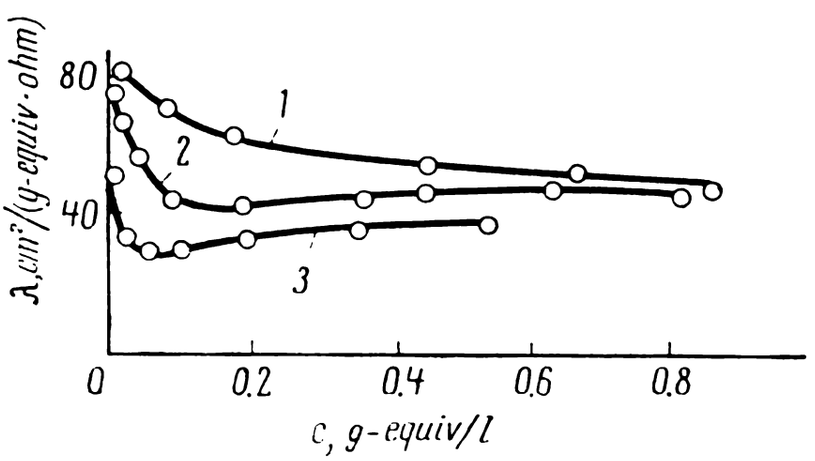


Fig. 13.5. Dependence of equivalent electric conductivity λ of soap solutions on concentration *c* (at 18 °C):
1—potassium caprylate; *2*—potassium laurate; *3*—potassium oleate

es and, as a result, the surface tension drops, reaching a minimum constant value at a point which corresponds to CCMF.

Several factors can affect CCMF in surfactant solutions. CCMF decreases as the molecular weight of a hydrocarbon chain of a surfactant grows because in this case, true solubility diminishes and the tendency of surfactant molecules to associate increases. The temperature effect on CCMF differs for ionogenic and non-ionogenic surfactants. For ionogenic surfactants, CCMF usually increases with temperature owing to the disaggregating action of the thermal motion of molecules. But this effect is not strong because it is weakened by hydrophobic interactions which cause an increase in the entropy of a system. Therefore, the effect of temperature on CCMF is the weaker, the more pronounced are the hydrophobic properties of soaps. For non-ionogenic surfactants, CCMF always decreases with an elevation of temperature because then hydrogen bonds between the oxygen atom of an ether and water molecules are broken, hydroxyethylene chains dehydrate, and their mutual repulsion, being a hindrance to aggregation, decreases.

Micelles can be formed not only in aqueous colloidal surfactant solutions, but also in solutions of surfactants in hydrocarbons. In this case, surfactant molecules in a micelle are oriented by their polar groups into a micelle, and by their hydrocarbon ends, towards

a solvent. However, surfactants usually produce molecular solutions in ethanol because, by its polarity, ethanol is between water and hydrocarbons, and therefore it is a solvent for both polar and non-polar parts of surfactant molecules.

3. STABILIZING ACTION OF SURFACTANTS

The stabilizing action of surfactants is determined by their ability to be adsorbed at the interface. Owing to high surface activity, the surfactant concentration in the surface layer is tens of thousands of times higher than the volume concentration. Non-polar groups associate in adsorption films, like in surfactant micelles. The structure of the adsorption layer depends on the nature of a surfactant and of the interface, the degree of surface filling, and the introduction of various additives into a medium. A change in the structure of the adsorption layer affects its protective properties.

Surfactant adsorption layers lyophilize and, in aqueous solutions, hydrophilize the surface as a result of which repulsive forces develop as particles approach one another. For ionogenic surfactants, this is the electrostatic repulsion of electric double layers described in the DLVO theory which was considered in Chap. 9. For non-ionogenic surfactants, electrostatic repulsion, as a rule, is of no importance; the stabilization of dispersed systems by these substances is among the unsolved problems in colloid chemistry.

The following concepts, evolved for non-ionogenic surfactants and for polymer adsorption layers, seem to be the most promising.

As particles approach one another to a distance which is less than double the thickness of the adsorption layer, these layers overlap (interpenetrate) and the concentration of non-ionogenic surfactants increases in the overlap region in comparison with its value in the adsorption layer. In this case, if the medium is a good solvent for a substance which forms the adsorption layer, osmotic pressure originates in a similar way as in swelling. This pressure can be a function of a change in the entropy or enthalpy of a system in the overlap region, depending on the nature of a non-ionogenic surfactant and of a solvent. In the first case, entropy drops owing to a diminution in the number of conformations of stabilizer flexible chains in this region. In the second case, contacts between water molecules and polar groups of non-ionogenic surfactants are replaced by contacts between non-ionogenic surfactant molecules in the overlap region, i.e., the adsorption layer is dehydrated and the enthalpy of a system grows. A drop in entropy or a growth in enthalpy makes the state of approached particles unstable and causes the inflow of a liquid from the solution volume to the overlap region, i.e., it induces positive disjoining pressure (Fig. 13.6). Thus, the adsorption

layers of non-ionogenic surfactants or of polymers prevent particles from sticking together and make a system aggregatively stable.

Proceeding from the concepts of the role of osmotic forces in the stabilization of dispersed systems, the German scientist E. Fisher

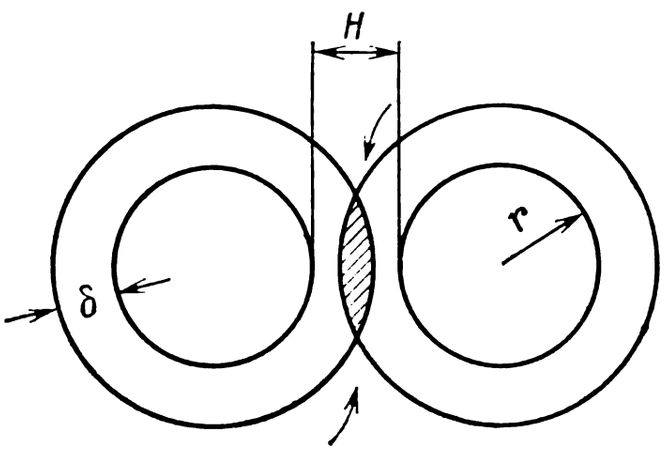


Fig. 13.6. Scheme illustrating the interaction of the adsorption layers of non-ionogenic surfactants:
r—particle radius; δ—thickness of the adsorption layer; *H*—interparticle distance

proposed an equation which makes it possible to calculate repulsive energy U_{osm} as particles approach one another to a distance less than 2δ:

$$U_{osm} = 2BN_A c^2 V_\delta kT \qquad (13.1)$$

where B = coefficient which characterizes the interaction between the molecules of a substance being dissolved and the molecules of a solvent;

N_A = Avogadro number;

c = concentration of a non-ionogenic surfactant in the interfacial layer;

V_δ = volume of the overlap region that can be calculated if the particle radius, the thickness of the adsorption layer δ of a non-ionogenic surfactant and the interparticle distance are known.

As Eq. (13.1) shows, repulsive energy is the greater, the higher is the concentration of an adsorptive in the interfacial layer. It grows also with the volume of the overlap region. Moreover, repulsive energy depends on the sign and value of coefficient B. In good solvents, when B is greater than zero, positive disjoining pressure originates and stabilizes a system. If a medium is a poor solvent for a substance which forms the adsorption layer, B is less than zero and disjoining pressure is negative, i.e., the medium flows out of the overlap region. In this case, the osmotic effect, together with intermolecular attractive forces, promotes the aggregation of particles. Lastly, when B is equal to zero, repulsive energy is equal to zero.

Even if there is no interaction with the solvent when B is less than or equal to zero, adsorption layers form a steric barrier that prevents particles from approaching one another to a sufficiently small distance at which intermolecular attractive forces become considerably strong. Of course, effective steric stabilization occurs only when adsorption layers are saturated and the molecules forming them cannot desorb when particles collide with one another. For such sterically stabilized systems, coagulation with direct particle contact is impossible, and only distant aggregation is possible.

4. SOLUBILIZATION IN SURFACTANT SOLUTIONS

Solubilization is an important property of surfactant solutions that is connected with their micellar structure.

When almost water-insoluble organic substances (aliphatic and aromatic hydrocarbons, oil-soluble dyes, etc.) are added to sufficiently concentrated surfactant solutions, these substances can dis-

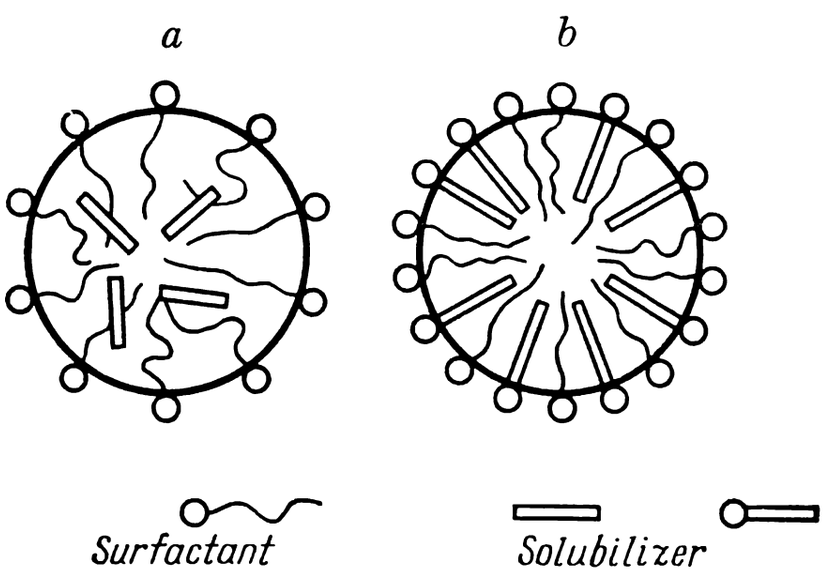


Fig. 13.7. Schematic illustration of the solubilization of hydrocarbons (*a*) and polar organic substances (*b*) in surfactant micelles

solve colloidally, or *solubilize*. Almost clear, thermodynamically equilibrium solutions are formed as a result of such solubilization. A substance which dissolves in surfactant solutions is known as a *solubilizer*.

The solubilizing ability of various surfactants is very diverse. The amount of a colloidally dissolved organic substance in homologous series of surfactants increases as a hydrocarbon radical becomes longer, and also proportionally to the concentration of a surfactant solution in the region of spherical micelles; it grows sharply when plate-like micelles are formed. Solubilization depends also on the molecular structure of a solubilizer. For example, if hydrocarbons are used as solubilizers, colloidal solubility increases as their mole-

cular weights decrease. Solubilization usually grows when polar groups are introduced into a solubilizer.

According to present views, solubilization is dissolution of organic substances in surfactant micelles. Solubilization mechanisms may be diverse. Non-polar hydrocarbons dissolve in a micelle nucleus (Fig. 13.7*a*), whereas polar organic substances (alcohols, amines) are oriented in micelles in a way that their hydrocarbon chains are directed into micelles, and polar groups, towards the aqueous phase

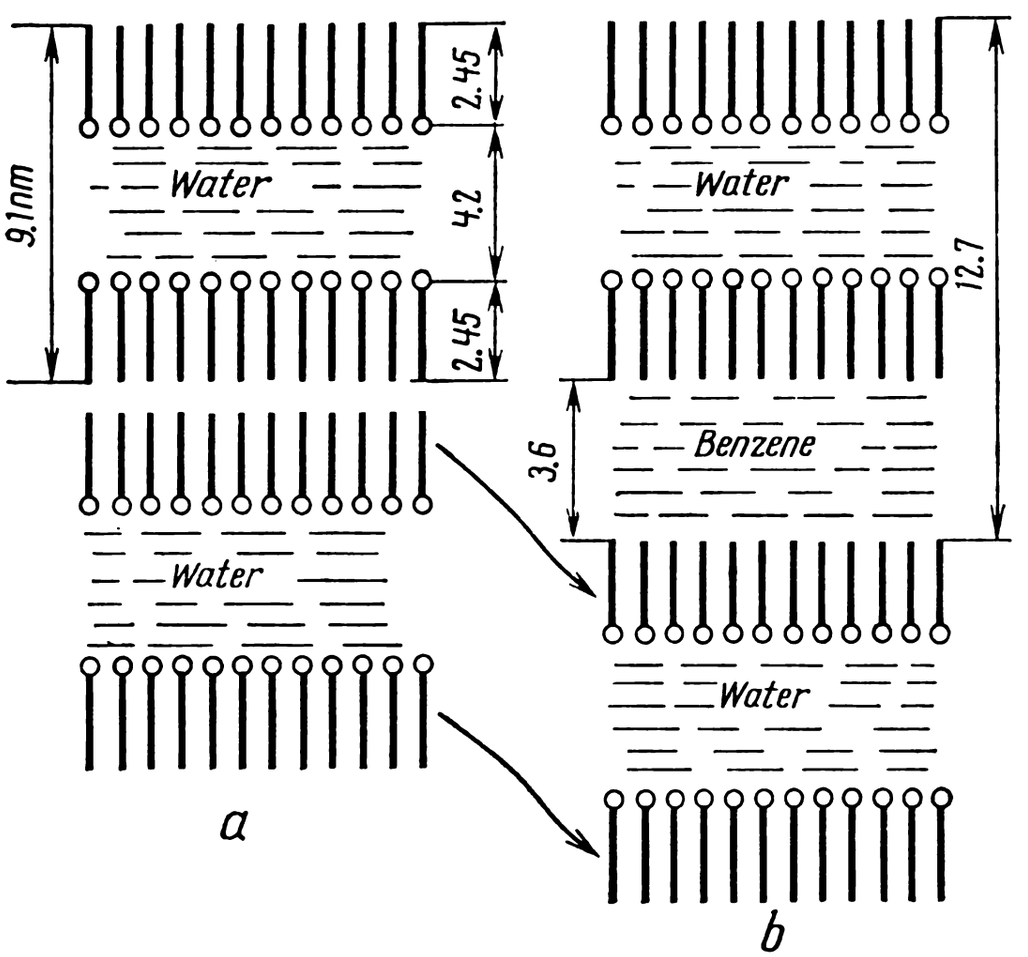


Fig. 13.8. Solubilization of benzene in a sodium oleate micelle:
***a*—micellar solution before solubilization; *b*—the same after solubilization**

(Fig. 13.7*b*). There is another mechanism of solubilizing non-ionogenic surfactants which contain polyhydroxyethylene groups. Molecules of a solubilizer (e.g., phenol) do not penetrate deep into micelles, but are arranged at their periphery, between folded hydroxyethylene chains, apparently forming a hydrogen bond with the oxygen atom of the ether.

In solubilization, the micellar weight of surfactants grows due not only to the incorporation of solubilizer molecules, but also to an increase in the number of surfactant molecules in a micelle. Such a rearrangement of micelles occurs because the micelle nucleus becomes more hydrophobic upon hydrocarbon solubilization, and there-

fore the number of surfactant molecules constituting a micelle must also increase in order to maintain equilibrium.

In solubilization in plate-like micelles, the organic substance penetrates into a micelle, arranging itself between the hydrocarbon ends of soap molecules and thus drawing apart layers of molecular chains. Such a viewpoint is confirmed by X-ray diffraction analysis which has shown that the distance between soap molecules in a micelle increases upon solubilization. A change in the structure of plate-like micelles upon solubilization is represented in Fig. 13.8.

The solubilization phenomenon is important in polymerizing unsaturated hydrocarbons in emulsions when latices are being synthesized. In this case the polymerization occurs mainly within or on the surface of soap micelles in which unsaturated hydrocarbon is solubilized, rather than in the drops of this hydrocarbon.

Reverse solubilization, i.e., the colloidal dissolution of water in oils in the presence of the appropriate colloidally oil-soluble surfactants, is of great importance in the food industry, particularly, in margarine production.

5. PRACTICAL IMPORTANCE OF COLLOIDAL SURFACTANT SOLUTIONS

Colloidal surfactants are of great practical importance, and soaps or soap-like substances are used in almost all the sectors of the national economy owing either to the formation of micelles in solutions or to high surface activity, i.e., the ability of their molecules to form surface adsorption layers.

The importance of surfactants in improving the wetting of surfaces with water, in obtaining stable emulsions and foams, and in flotation processes was dealt with in Chaps. 6 and 12. Let us now discuss some other applications of colloidal surfactants in technological processes.

Let us consider soap detergency in somewhat greater detail (see Chap. 6); it is among the processes in which the ability of colloidal surfactants to form adsorption layers is cardinal.

Solid or liquid impurities are very difficult to remove from the surface of textile fibres with pure water even at elevated temperature and under intensive mechanical action. However, this can be done rather easily if a surfactant solution is used for laundering. Surfactant detergency is connected with several effects.

1. When surfactants are present in water, the surface tension of a solution decreases and a textile is better wetted with a detergent liquid. This helps the liquid to penetrate into the thin capillaries of a dirty textile into which pure water cannot penetrate.

2. Soap molecules adsorb on the fibre surface and on the particles of solid or liquid impurities, create a well hydrated adsorption layer, and induce the origination of disjoining pressure. As a result, impurity particles tear away from the fibre surface and pass over to the detergent liquid.

3. Adsorption films on the surface of impurity particles impart high aggregative stability to these particles and prevent them from adhering to the fibre surface in another place.

4. In the presence of surfactants, foam is formed in a detergent liquid, promoting the mechanical removal of impurities or the flotation of those impurities whose particles adhere to air bubbles owing to low wettability.

5. Surfactant detergency is to a certain extent connected with the ability of impurity particles, especially if they are unctuous, to solubilize in surfactant solutions. This is confirmed by the fact that detergency is often detected only at concentrations which are higher than CCMF.

6. TANNINS AND DYES

Colloidal surfactant properties are exhibited by almost all the tanning agents that are the derivatives of polyatomic phenols in which polar and ionogenic groups are phenolic and carboxylic groups. Micelles can appear in aqueous solutions of tannins as a result of not only the aggregation of molecules along hydrophobic parts, but also the formation of hydrogen bonds. According to A. Mikhailov, the molecular weight of association products in tanning solutions is about 20,000 whereas the molecular weight of tannins is within the range of 1000-2000. It follows that a micelle consists of 10-20 molecules.

Among the dyes which exhibit all the characteristics of colloidal surfactant solutions are synthetic dyes, e.g., benzopurpurine and nocturnal blue. The ionogenic groups of colloidal dyes are carboxylic, phenolic, sulpho, amino, and other groups. Solutions of these dyes are similar to compounds having high molecular weight: they have rather high aggregate stability, and the precipitate formed when electrolytes are added is capable of undergoing dispersion in pure water. Solutions of these dyes exhibit the same anomalies of electric conductivity and osmotic pressure as the solutions of soaps and tannins. S. Lipatov has shown that, owing to the large dimensions of dye molecules, association in dye solutions occurs at a higher rate than in soap solutions, and greatly depends on the concentration, temperature and pH of a system, the presence of electrolytes, and other factors. Many dyes, like soaps, produce colloidal solutions in water, but form molecular solutions in ethanol.

14

NATURE AND SOME PROPERTIES OF SOLUTIONS OF MACROMOLECULAR SUBSTANCES

Solutions of macromolecular substances are true solutions, being thermodynamically stable, reversible, and not requiring a stabilizer. Particles in such solutions do not consist of many small molecules, as is the case with colloids, but are individual molecules though very large ones. This is what distinguishes solutions of high-molecular-weight compounds from those of low-molecular-weight substances. Nevertheless, several scientists (H. Kruyt, H. Bundenberg de Jong, I. Zhukov, and others) relate solutions of macromolecular substances to colloidal ones. Some authors call the substances dissolved in them reversible colloids (Kruyt, Bundenberg de Jong) while others, molecular colloids (I. Zhukov). The main properties inherent in lyosols are attributed, in the case of solutions of high-molecular-weight substances, only to the huge dimensions of molecules which are almost as large and occasionally even larger than colloidal particles. Therefore, solutions of high-molecular-weight substances could scarcely be related to colloidal solutions.

But there are some causes which make solutions of high-molecular-weight substances similar to colloidal systems. For example, solutions of high-molecular-weight compounds in bad solvents contain molecules (or molecular aggregates) which are folded into a compact coil having a well defined interface. In essence, they represent a separate phase. Such solutions of high-molecular-weight compounds can be called colloidal systems. Furthermore, sufficiently large associates of macromolecules existing for an infinitely long time originate in concentrated solutions of high-molecular-weight substances. These particles can also be regarded as a second phase or, at least, as the nucleus of this phase. Lastly, solutions of high-molecular-weight substances have several lyosol properties because of the large dimensions of their molecules; therefore, many problems concerning colloidal solutions and solutions of high-molecular-weight substances can be considered together.

Thus, the nature and properties of solutions of high-molecular-weight substances must be dealt with even briefly in this textbook, attention being drawn mainly to the systems and phenomena which resemble most closely colloidal ones. But before discussing solutions of high-molecular-weight substances, let us dwell briefly on high-molecular-weight substances and consider the specific features of their molecular structure.

1. GENERAL INFORMATION ON MACROMOLECULAR SUBSTANCES

Among macromolecular substances* are those which consist of large molecules (macromolecules) having a molecular weight of at least 10,000-15,000. The molecular weight of natural high-molecular-weight compounds often reaches several million. Macromolecules are very large in comparison with ordinary molecules. For example, the length of an ethane molecule is only several angstroms while that of the linear molecules of rubber and cellulose reaches 4000-8000 Å (when the lateral size is 3-7.5 Å). A model of such molecules may be threads having a length of 800-1600 mm and a diameter of 1 mm.

Macromolecular substances are non-volatile and are incapable of being distilled owing to their high molecular weight. For the same reason, high-molecular-weight substances are very sensitive to the action of external factors. Macromolecules readily disintegrate under the action of traces of oxygen and other destructive agents. The following example shows why there is a difference in the sensitivity to chemical effects of low- and high-molecular-weight substances. Suppose that one oxygen molecule is enough to split one molecule of substance into two. Then, for a low-molecular-weight substance having a molecular weight of, say, 100, the amount of oxygen needed for making such a split should be 32 per cent of its mass. If the molecular weight of a substance being oxidized is 100,000, the oxygen needed for the same purpose will constitute only 0.032 per cent of its mass; this is only 32×10^{-5} g of oxygen per 1 g of a substance, i.e., an amount which is detected with great difficulty even when the most precise analytical balance is used. Most macromolecular substances soften gradually with an elevation of temperature and do not have a definite melting point. The decomposition point of these substances is lower than the melting point. Consequently, high-molecular-weight substances can be only in a condensed state.

The properties of high-molecular-weight substances depend not only on the dimensions of molecules, but also on their shape.

* They also include polymers, i.e., high-molecular-weight substances which are obtained by polymerization or condensation, have a linear molecular structure, and often high elasticity.

Macromolecular compounds having isodiametric molecules (such as hemoglobin or glycogen) are usually powder. They do not swell on dissolution, their solutions do not have high viscosity even at relatively high concentrations, and they obey Poiseuille's viscosity law, Einstein's diffusion law and van't Hoff's law of osmotic pressure.

High-molecular-weight compounds having asymmetric stretched-out molecules (e.g., gelatin, cellulose and its derivatives, natural and synthetic rubbers) swell very much on dissolution and form high-viscous solutions which do not obey the regularities applicable to solutions of low-molecular-weight substances.

A characteristic feature of high-molecular-weight substances having linear molecules is a fibrous structure which causes the anisotropy of properties and high mechanical strength. Therefore, such substances can form fibres and films. Some polymers have a very valuable property: high elasticity.

Natural macromolecular substances. Among natural high-molecular-weight substances are such organic substances as proteins, higher polysaccharides and natural rubber, which are extremely important in biology and technological processes.

Proteins are extremely complex high-molecular-weight compounds. They are the main substance of the protoplasm of human, animal and plant cells. All enzymes, many hormones and viruses also are proteins. Among the proteins used in technological processes are gelatin, casein, and egg albumin.

Protein molecules consist of amino acids, contain ionogenic groups (—COOH, —NH_3OH), and have amphoteric properties. Proteins dissolve in alkaline solutions, and some of them dissolve in water and diluted solutions of salts and acids. Protein solutions are very unstable with respect to temperature: on heating, many proteins are denatured and become insoluble. Proteins are precipitated from solutions by electrolytes, ethanol, and acetone. So far, many proteins cannot be synthesized owing to their complex structure.

Higher polysaccharides include starch and cellulose.

Starch consists of glucose residues and is not an individual substance, but a mixture of polysaccharides which differ not only in dimensions of their macromolecules but also in structure. Starch is among the most important photosynthetic products which are formed in the green parts of plants; it constitutes the bulk of bread, potatoes, and cereals. Starch swells and becomes pasty at a definite temperature in water, forming an apparently homogeneous thick liquid; this starch paste is widely used in technological processes as glue, in sizing and finishing textiles, in pasting paper, and so forth. Dextrin, syrup, and glucose are obtained from starch by hydrolysis.

Cellulose is the main constituent of a plant organism, making it strong and elastic. Cellulose also consists of long chains which are

made out of glucose residues, but which are connected with one another somewhat differently than in a starch molecule. Attempts to synthesize cellulose failed so far, and therefore it is obtained from wood, straw, and other plant materials by hot treatment with solutions of substances which dissolve lignin and other impurities contained in these materials. Cellulose is widely used for making paper. Cotton and other types of plant fibre, being almost pure cellulose, are used in the textile industry. Cellulose derivatives, i.e., cellulose nitrate, cellulose acetate, and other ethers and esters of cellulose, are used for making photographic films and artificial fibre.

Natural rubber is an extremely valuable material which possesses high elasticity. It is obtained from the latex of rubber plants. It is a hydrocarbon whose macromolecules consist of isopentene (isoprene) residues. It dissolves in hydrocarbons and possesses plasticity which is exhibited especially well at elevated temperature. Rubber vulcanizes when it is heated together with a small amount of sulphur: its molecules become chemically bound with one another by sulphur bridges. Vulcanized rubber loses the ability to dissolve and soften on heating, but it retains elastic properties. When rubber is heated with a large amount of sulphur, it loses elasticity and forms a solid vulcanizate, known as ebonite, as a result of the formation of a large number of cross-links between rubber molecules.

Synthetic macromolecular substances. Besides natural high-molecular-weight substances, several synthetic macromolecular products are now used in technological processes and everyday life. They include synthetic rubber and synthetic polymers. These products, being extremely diverse in chemical composition and properties, are perfect substituents of natural high-molecular-weight substances and are often applied in a completely new way. For example, they are used as a substance for obtaining plastics, as plexiglas, as ion-exchangers (ionites) for purifying water and isolating individual substances from mixtures, as substances for making parts of planes and automobiles and even bodies of low-tonnage ships. The production of synthetic high-molecular-weight substances has considerably outstripped the production of not only traditional construction materials, but also such comparatively new materials as aluminium and magnesium alloys.

Among the advantages of synthetic high-molecular-weight substances is that they can be obtained with preset properties, i.e., strength, elasticity, chemical stability, and a dielectric constant, by selecting suitable starting materials and controlling a technological process. Synthetic high-molecular-weight substances can be used to produce articles by direct moulding without losing material as a shaving and without the subsequent treatment of articles.

Synthetic high-molecular-weight substances are widely used also because there are unlimited resources of raw materials needed for producing them. To synthesize macromolecular substances, use is made of the simplest products of oil refining and coal processing, acetylene, and the wastes of several industries.

Synthetic rubbers include industrially produced polybutadiene, polychloroprene, butadiene-styrene and butadiene-nitrile copolymers and several other products. The molecular structure of these substances is considered in all the textbooks of organic chemistry.

Besides synthetic rubbers proper which are capable of being vulcanized in the same way as natural rubber owing to double bonds in their macromolecules, there are several synthetic polymers which do not have this ability, but possess high elasticity. They include, for example, polyisobutylene which is the product of low-temperature polymerization of isobutylene. Polyisobutylene films are gas-impermeable and do not change under the action of air and ozone; as a result, polyisobutylene is widely used for making balloon sheaths, pilot balloons, and so forth. When isobutylene is copolymerized with a small amount (2-3 per cent) of diene, e.g., isoprene, products are obtained that already contain a small number of double bonds in their molecules. These products, which are capable of being vulcanized, have become known as butyl rubbers.

Polysiloxanes are very interesting new high-molecular-weight products which are used for thermally stable electric insulation. Polysiloxanes, like rubbers, possess high elasticity, but they are very strong and more stable to temperature because their main chain consists of silicon and oxygen atoms.

Synthetic polymers, which under ordinary conditions do not possess high elasticity, are polyethylene, polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polymethyl acrylate, polymethyl methacrylate, polystyrene, and several other well known products that are used for making articles out of plastics, films, and so forth. These substances are thermoplastic because they can soften and be moulded on heating. Synthetic polymers also include thermosetting resins which are fluid in the initial state and can irreversibly harden on heating as a result of chemical reactions. Among such resins are phenol-formaldehyde and urea-formaldehyde ones which are being used in technological processes for several decades now.

Among comparatively new polymers, let us name only polyamides and polytetrafluoroethylene.

Polyamides are produced by the polycondensation of diamines with dicarboxylic acids, e.g., by the condensation of hexamethylene diamine and adipic acid, or the polymerization of ω-amino acids. Polyhexamethylene adipamide is obtained as a result of these reactions. In the United States, the artificial fibre nylon is produced

from polyhexamethylene adipamide. By its properties, it is similar to woolen and silk fibres, and is even better. The exceptionally high tensile strength of the nylon fibre, reaching 4000-4500 kgf/cm^2, is due to the polarity of polyhexamethylene adipamide molecules, the formation of hydrogen bonds between individual molecular chains, and the fact that polyamide is mainly in an oriented, crystalline state in a stretched fibre. The polyamide fibre, capron, produced in the Soviet Union by polymerizing caprolactam, is similar in properties to nylon.

Chemistry of fluorine compounds owes its rapid development to polytetrafluoroethylene production. The molecules of this polymer are non-polar because highly electronegative fluorine atoms are arranged symmetrically in them. Polytetrafluoroethylene crystallizes rather readily owing to the regular linear structure of its molecules. Polytetrafluoroethylene is one of the most highly melting crystalline polymers. But the temperature at which it becomes brittle is very low. As a result, polytetrafluoroethylene articles can be used in a very wide temperature range. Polytetrafluoroethylene excels all the hitherto known polymers by its thermal and chemical stability and dielectric properties.

Inorganic macromolecular substances. Besides organic high-molecular-weight compounds which have been studied well, there are also

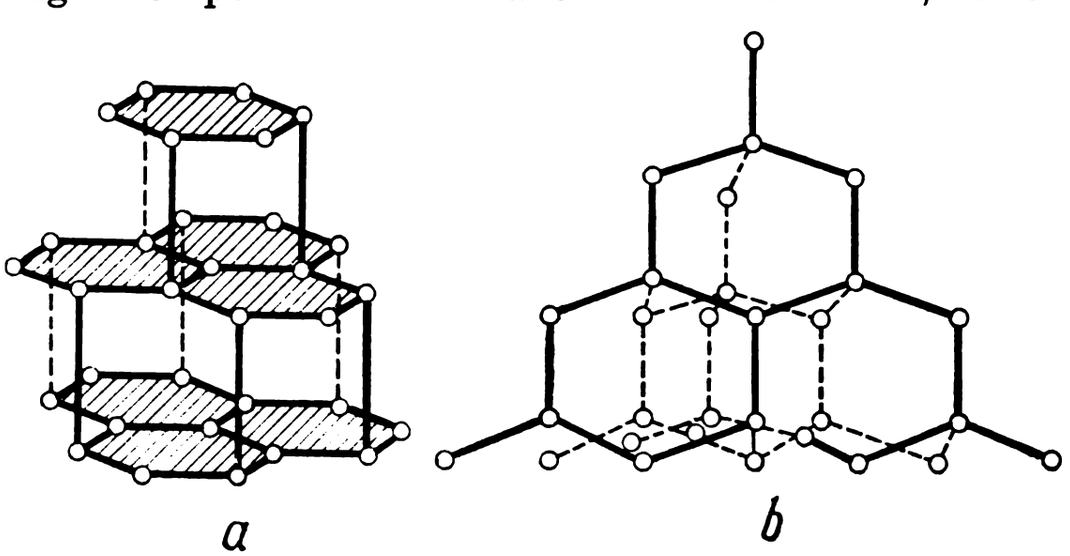


Fig. 14.1. Structure of graphite and a diamond:
a—planar lattices of graphite; *b*—three-dimensional structure of a diamond

inorganic high-molecular-weight substances though their molecular structure and the properties of their solutions still have not been sufficiently investigated.

Inorganic macromolecular substances having a chain molecular structure include, for example, a sulphur modification ("plastic" sulphur) which is obtained by rapidly cooling a sulphur melt heated to above 300 °C. High-molecular-weight sulphur possesses rubber-like elasticity because of its chain molecular structure.

Polyphosphonitrile chloride is also an inorganic high-molecular-weight substance.

An example of two-dimensional inorganic high-molecular-weight substances is ordinary mica whose molecules are plate-like, aluminosilicates which constitute clay, and graphite whose crystals are made out of carbon hexagons arranged one under another as individual planes. Owing to the rather large distance between layers and the unstable bond between them, it can be assumed that every plane in graphite is a molecule.

An example of a three-dimensional inorganic high-molecular-weight compound is a diamond which consists of carbon atoms. In a diamond crystal, every carbon atom is bound to four adjacent carbon atoms. A diamond crystal can be regarded as a gigantic molecule which lacks several properties characteristic of ordinary molecules. As a result of such a structure, a diamond is incapable of either swelling or dissolving in any solvent, and it possesses very high hardness. Graphite and diamond structures are shown in Fig. 14.1.

Intermediate systems. Solutions of intermediate-type substances exhibit properties of either typical sols or of solutions of high-molecular-weight compounds, depending on the conditions under which they are obtained. Such substances are oxides and hydroxides of elements which form weakly acidic or amphoteric compounds, e.g., silicon hydroxide.

The freshly prepared solutions of these oxides and hydroxides are similar in many respects to the solutions of high-molecular-weight compounds. These substances are precipitated from solutions when an electrolyte is added, but the precipitate readily passes into a colloidal solution again if the coagulant is removed. Such precipitation and dispersion of, say, stannic oxide can be effected any number of times. The action of electrolytes on the solutions of such substances and the effect of the valency of an ion which causes a drop in the ζ-potential of particles are far less considerable than they are with respect to typical colloidal systems, e.g., sols of metals and their sulphides. The relative viscosity of solutions of such substances is considerably higher than that of ordinary sols. Lastly, their solutions can produce gels which are very similar in properties to those of macromolecular substances.

It follows that such solutions contain macromolecules. For example, it can be assumed that a molecule of orthosilicic acid in its freshly prepared solution has the following structure:

$$(HO)_3SiO-[Si(OH)_2-O]_n-Si(OH)_3$$

The structure of molecules in the solutions of ferric hydroxide, aluminium hydroxide and other solutions that exhibit colloidal

properties can probably be represented also in that way. However, such solutions are known to acquire typical properties of ordinary colloidal systems when they are allowed to stand or when electrolytes are added to them. This phenomenon with respect to liquid glass can be attributed to the presence of hydroxyl groups in the molecules of orthosilicic acid; as a result, molecules become cross-linked with chemical bonds, for example, when an acid is added. If the solutions are diluted enough, individual micelles may be formed by the cross-linking of the regions of the same flexible macromolecule, and silicic acid acts as a stabilizer.

If the solutions are sufficiently concentrated, a three-dimensional network is formed as a result of macromolecular cross-linking and the solution becomes an irreversible gel. Such a phenomenon is very similar to condensation which occurs when phenol-formaldehyde resins solidify. The difference is that gels of silicic acid have a crystalline structure after drying and heating.

Intermediate systems, which are between solutions of macromolecular compounds and typical colloidal solutions or which are capable of passing from one class of solutions to another, should not be confused with colloidal surfactant solutions that exhibit properties of true solutions under some conditions, and typical sol properties under others.

2. POLYDISPERSITY AND MOLECULAR WEIGHT OF MACROMOLECULAR SUBSTANCES

Polymer polydispersity. In polymerization or polycondensation macromolecules of diverse dimensions are usually obtained, i.e., a

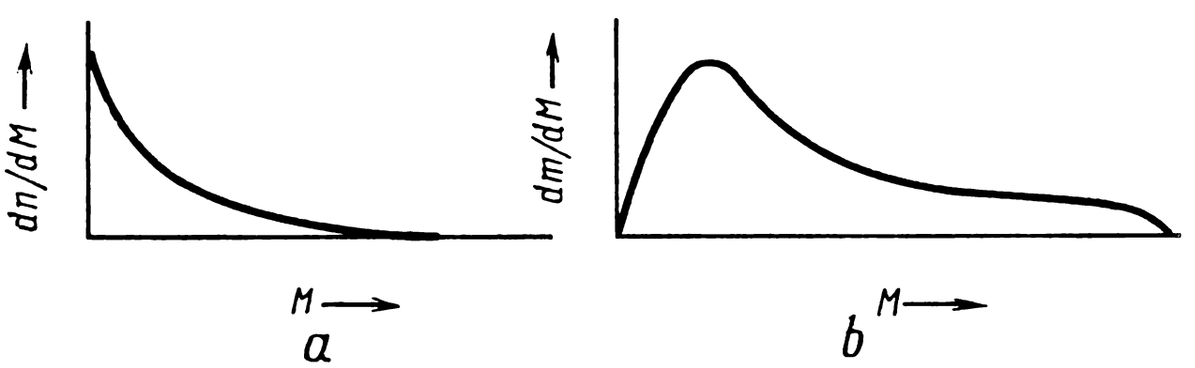


Fig. 14.2. Curves for distribution of fractions of macromolecular compounds: *a*—according to the number of particles; *b*—according to the mass of macromolecules

polymer homologous series is formed owing to the difference in technological conditions. Therefore, we usually speak of the polydispersity of a high-molecular-weight substance which can be conveniently characterized by distribution curves similar to those considered in Chap. 3. Fig. 14.2 shows typical distribution curves for the same

polymer. One curve characterizes distribution according to the number (*a*), and the other, according to the mass of macromolecules (*b*). The two curves considerably differ in shape because small macromolecules, which are usually present in a large amount in the reaction product, constitute a rather small weight fraction.

The swelling and dissolution of macromolecular compounds, their physico-mechanical properties, and the properties of their solutions considerably depend on their polydispersity. Therefore the determination and control of polydispersity of high-molecular-weight substances are important in technological processes.

To obtain macromolecular products which are more homogeneous by the degree of their polymerization or by their molecular weight, they are usually fractionated by dissolution or precipitation.

Fractionation by dissolution is based on the dependence of the solubility of polymer homologues on molecular size: the smaller is a molecule, the better does a homologue dissolve. For fractionation, a macromolecular substance is first treated with a liquid which dissolves the low-molecular-weight members of a polymer homologous series; then, the product that remains is treated with a liquid which dissolves fractions of a higher molecular weight, and so forth. Instead, mixtures of two liquids, one of which is a good solvent for all fractions and the other does not dissolve them, are often used. By changing the ratio between these two liquids in mixtures with which extraction is successively effected, the product can be divided into any large number of fractions of a different molecular weight. The extracted fraction is precipitated from solutions obtained by fractional dissolution if a large amount of a non-solvent is added. For example, to fractionate cellulose nitrate, a mixture of water and acetone can be used, and to fractionate rubber, a mixture of ethanol and benzene can be employed.

Fractionation by precipitation is effected from a solution of a high-molecular-weight substance which contains all the fractions. Several fractions are successively precipitated by adding an increasing amount of a non-solvent to the solution. Of course, the molecular weight of all these fractions will be the smaller, the greater is the amount of a non-solvent added because fractions of the lowest molecular weight always possess the greatest solubility.

Completely homogeneous fractions in which all the molecules would have the same length can hardly be fractionated by either dissolution or precipitation because the difference in solubility (like in all the other physical properties) becomes very inconsiderable as the difference in the chain length diminishes.

Macromolecular substances often contain impurities: electrolytes and organic low-molecular-weight substances. Macromolecular substances are purified by dialysis. The techniques of dialyzing solutions of high-molecular-weight substances do not differ from those

of dialyzing typical colloidal systems. If only electrolytes are present in the aqueous solution of a product being purified, electrodialysis can be used to remove them. If a product is insoluble in a liquid selected for dialysis and can only swell in it, the macromolecular substance can be simply wetted and the liquid regularly changed instead of employing dialysis.

Methods of determining the molecular weight of macromolecular substances. Such properties of macromolecular compounds as strength, elasticity, the ability to swell and dissolve depend on their molecular weight (and likewise on their polydispersity). Therefore, it is important for a chemist dealing with macromolecular compounds to be able to determine their molecular weight.

The ordinary methods of determining the molecular weight of organic compounds are scarcely suitable for determining that of macromolecular compounds. Therefore, completely new methods of determining the molecular weight of these substances have been worked out, and many of them are similar to those employed for determining the numerical weight used in colloid chemistry. The underlying principles of these methods are given briefly below.

The methods of determining the molecular weight of macromolecular compounds can be divided into four groups.

1. *Chemical methods.* If a molecule of a high-molecular-weight compound has a known, strictly definite number of reactive groups (e.g., groups arranged at the end of a molecule), the quantitative estimation of these groups can serve as a method of determining the molecular weight. These methods are used in practice rather rarely owing to experimental difficulties. They are dealt with at length in the textbooks of the chemistry of high-molecular-weight substances.

2. *Thermodynamic methods* of determining molecular weights are based on the thermodynamic regularities characteristic of diluted solutions; they consist in determination of the molar fraction of a substance in the solution of a known concentration.

The molecular weight in this case is determined by osmotic pressure, by a drop in the freezing point of a solution (cryoscopic method), and by an elevation of the boiling point of a polymer solution (ebullioscopic method).

3. *Molecular-kinetic methods* are based on the movement of macromolecules relative to a solvent and consist ultimately in the determination of the appropriate friction force. The determination of the molecular weight by the diffusion rate, by the viscosity of solutions, and by ultracentrifugation belongs to this group of methods.

4. *The optical method*, being widely used now, is based on the measurement of the intensity of light scattering by solutions of high-molecular-weight compounds.

Experiments have shown that, among thermodynamic methods, the only suitable one is the method of determining molecular weight by osmotic pressure. Here, one does not come across difficulties which are encountered in determining the numerical weight of colloidal systems because solutions of high-molecular-weight compounds withstand purification well.

Cryoscopic and ebullioscopic methods are suitable only for determining the molecular weight of polymers having rather small molecules because, when the molecular weight of a solute in diluted solutions (to which the methods are applicable) is very high, the difference in freezing and boiling points is not perceptible.

Among the molecular-kinetic methods, the most reliable and theoretically substantiated one is the ultracentrifugation method. The method of determining the molecular weight by sedimentation equilibrium deserves particular attention because the calculation formula in this case does not include the time taken for analysis and the friction force; therefore, there are no arbitrary allowances for the particle shape that have to be made when other molecular-kinetic methods are used. Among the molecular-kinetic methods, the viscometric method is the most simple one although it is not very precise.

The dimensions of molecules of macromolecular substances whose molecular weight is about 10^6-10^7 (viruses, hemocyanin, etc.) can be determined also directly by electron microscopy.

Mean molecular weight. We have already seen that macromolecular substances consist of a mixture of molecules which differ in dimensions, but are built according to one and the same principle from the same monomeric residues. This concept of an individual high-molecular-weight substance considerably differs from that of an individual low-molecular-weight compound whose molecules have the same, strictly definite dimensions.

Since a high-molecular-weight substance is always a mixture of polymer homologues, i.e., molecules of a different weight, we can speak only of its mean molecular weight. This mean value depends on the experimental method used for finding it.

The molecular weight of polymers is usually expressed by the number-average and weight-average values, $\overline{M}_n$ and $\overline{M}_G$. The number-average value of the molecular weight is determined by the equation

$$\overline{M}_n = \sum n_i M_i / \sum n_i \qquad (14.1)$$

where n_i is the number of molecules which have a molecular weight of M_i. The number-average molecular weight is found by methods which make it possible to determine the number of molecules in the

test solution of a high-molecular-weight substance. They include osmotic, cryoscopic, and ebullioscopic methods.

The weight-average value of the molecular weight is found by the equation

$$\overline{M}_G = \sum G_i M_i / \sum G_i = \sum n_i M_i^2 / \sum n_i M_i \qquad (14.2)$$

where G_i is the mass of a fraction having a molecular weight of M_i. The weight-average molecular weight is determined by methods which make it possible to establish the average dimensions of molecules in a solution. Such methods are, for example, the determination of the molecular weight by the diffusion rate, sedimentation in an ultracentrifuge, and light scattering.

It is quite clear that $\overline{M}_n = \overline{M}_G$ for a monodispersed product. For a polydispersed substance, $\overline{M}_n < \overline{M}_G$ because $\overline{M}_G$ grows with an increase in polydispersity. The greater is the difference in the molecular weights of fractions of a macromolecular substance, the higher should be the ratio $\overline{M}_G/\overline{M}_n$. The quantity $\overline{M}_G/\overline{M}_n$, which characterizes the polydispersity of a high-molecular-weight substance, is known as the *polydispersity index* or the *polydispersity coefficient.*

When a high-molecular-weight substance contains a small amount of a low-molecular-weight fraction, the values of $\overline{M}_n$ and $\overline{M}_G$ differ inconsiderably from one another, and the ratio $\overline{M}_G/\overline{M}_n$ appro x imates unity. When the content of a low-molecular-weight fraction is large, the differences between the values of $\overline{M}_n$ and $\overline{M}_G$ are great, and the ratio $\overline{M}_G/\overline{M}_n$ is very high. The calculated values of $\overline{M}_n$ and $\overline{M}_G$ for two mixtures of molecules having weights of 100,000 and 1000 are given below:

Content of the fraction having a molecular weight of 100,000, %	99	50
Content of the fraction having a molecular weight of 1000, %	1	50
$\overline{M}_G$	100,000	99,000
$\overline{M}_n$	99,000	50,500
$\overline{M}_G/\overline{M}_n$	1.01	1.96

It is expedient to determine $\overline{M}_n$ and $\overline{M}_G$ also when a high-molecular-weight substance is more or less monodispersed. If, in this case, a considerable discrepancy is observed between $\overline{M}_n$ and $\overline{M}_G$, it means that molecules have a branched structure.

3. STRUCTURE OF MACROMOLECULES AND STRUCTURE OF MACROMOLECULAR SUBSTANCES

Molecules of high-molecular-weight substances can be either linear or branched, and molecular chains can be rather long, reaching more than 1 μm. The linear shape of macromolecules is what determines typical polymer properties: rubber-like elasticity, the ability to form strong films and threads, to swell, to produce viscous solutions on dissolution, and so forth.

Besides chain molecules, polymers having a three-dimensional structure can be obtained either under definite technological conditions or by special treatment. Of course, the concept of a molecule means nothing to three-dimensional polymers because spatial networks can have very large dimensions. A typical example of a polymer having a three-dimensional structure is vulcanized rubber which consists of rubber molecules that are cross-linked with sulphur bridges.

The properties of chain macromolecules are considered below because solutions containing such molecules are of the greatest interest in theory and practice. Polymers having a three-dimensional structure are incapable of dissolving, and therefore the properties of molecular networks are not considered in this textbook.

Flexibility of linear macromolecules. Until recently, some scientists considered linear macromolecules to be rigid. But experiments of the last decades have shown that these molecules are flexible in most cases.

To understand the cause of flexibility of linear macromolecules, let us consider the structure of an ethane molecule. It can be represented as two groups of $-CH_3$ connected by a single bond. We know from organic chemistry that $-CH_3$ groups in an ethane molecule are capable of rotating about a single C—C bond. This accords well with the fact that, for example, symmetric dichloroethane does not have isomers. However, at low temperature, free rotation about the C—C bond is hindered because not all the possible positions of $-CH_3$ groups relative to one another are equivalent energetically. Such non-equivalence occurs because, as one $-CH_3$ group turns relative to another, distances between hydrogen atoms of both groups change. This causes a change in the energy of interaction between the $-CH_3$ groups. Therefore, at low temperature, the $-CH_3$ groups do not rotate about the C—C axis, but only oscillate rotatively at a rather small angle. The energy barrier can be overcome only at a sufficiently high temperature owing to an increase in kinetic energy, and the $-CH_3$ groups will freely rotate about the bond that connects them.

The height of a potential rotation barrier is, of course, the higher, the greater is the difference between the maximum and minimum

values of the interaction energy of atoms or atomic groups as they rotate relative to one another. Free rotation is hindered the greater, the larger are the atoms bound with carbon atoms. Experiments have shown that free rotation about the C—C bond requires an activation energy of the order of 3000 cal/mol even when carbon atoms are bound to rather small hydrogen atoms.

Rotation is possible if carbon atoms are connected with a single bond. There can be no rotation of $=CH_2$ or $\equiv CH$ groups (e.g., in

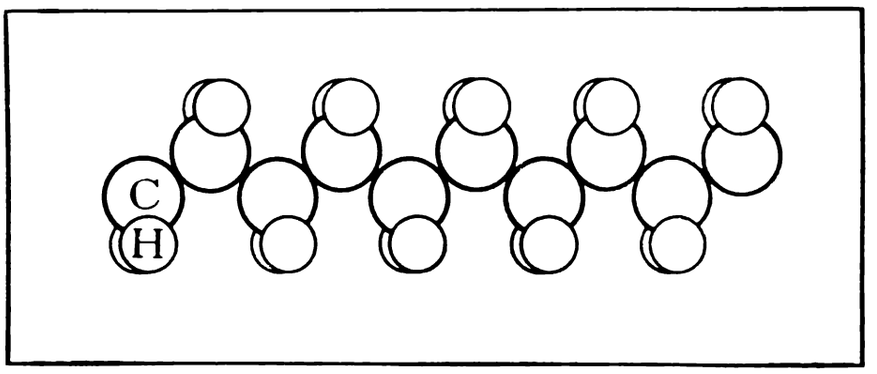


Fig. 14.3. Structure of a linear hydrocarbon chain

molecules of ethylene or acetylene), i.e., rotation about a double or triple bond. At the same time, the presence of a double bond in a hydrocarbon chain promotes the mobility of atoms or groups adjacent to this bond and connected with a single bond. For example, in the $-CH_2-CH=CH-$ group, the potential barrier which corresponds to rotation about the CH_2-CH bond is lower than the energy barrier for rotation about the CH_2-CH_2 bond by 500 cal/mol.

Let us now consider a certain linear macromolecule, say, a saturated hydrocarbon chain. Each carbon atom in such a chain is bound by single bonds with two other carbon atoms and with two hydrogen atoms. The chain is arranged not on a plane, but in space, and has a zig-zag shape in an ideal case. The angle between every three adjacent carbon atoms has a constant value of 109°28′, and a considerably large amount of energy is required for changing it. The structure of a saturated hydrocarbon chain is schematically illustrated in Fig. 14.3.

W. Kuhn, H. Mark and E. Guth have shown that a hydrocarbon chain is flexible owing mainly to the rotation of some parts of a chain relative to others about a single valency bond which connects adjacent carbon atoms. Since there are many such bonds in a macromolecule, it becomes clear how exceptionally flexible hydrocarbon bonds are.

As Kuhn, Mark and Guth believed, in the first approximation, rotation about C—C bonds in a macromolecule can occur quite freely, and hydrocarbon molecules are very flexible threads which can assume any shape that is compatible with the constancy of the valency

angle. But Ja. Frenkel and S. Bresler have shown that, like for an ethane molecule, certain activation energy is required in this case as well, i.e., an energy barrier which depends on the nature of atoms constituting a chain must be overcome. In other words, rotation about the C—C bond is possible only at sufficiently high temperature. Such a dependence of the freedom of rotation on temperature becomes clear from the following considerations.

As temperature rises, the energy of thermal motion grows, the latter being equal on the average to the product kT (where k is Boltzmann's constant, and T is absolute temperature) for every particle. As long as the quantity kT is considerably less than the energy barrier, atomic groups only rotatively oscillate near the equilibrium position. As temperature rises, the amplitude of these oscillations increases, and when the value of kT becomes commensurable with that of the energy barrier, rotation begins and molecules become flexible. Of course, an opposite phenomenon is observed when temperature drops, i.e., free rotation about a single bond becomes impossible and a molecule loses flexibility.

If a molecule can have several equilibrium positions instead of one, in the case of rotation about the C—C bond, a polymer represents an individual isomer in each position. M. Wolkenstein called such isomers rotational isomers. Apparently, ordinary polymers are mixtures of rotational isomers. These isomers differ from *cis*- and *trans*-isomers in that their energy barrier is rather low and they can readily convert into one another.

We have considered a linear macromolecule as a stretched zig-zag chain. Such a shape corresponds to the lowest potential energy of a molecule, and linear macromolecules tend to assume this shape at very low temperature. When molecular chains are stretched out, they orient better and can be packed compactly; that is what explains the ability of polymers consisting of linear macromolecules to crystallize on extension. As temperature rises, linear macromolecules can fold into coils owing to an increase in macromolecular flexibility, greater intensity of the thermal motion of individual units, and the impacts received from adjacent molecules. Since a linear macromolecule can be only in one maximally stretched-out state, whereas there are many conformations* which a macromolecule can assume on folding, all flexible polymer molecules will be coils at sufficiently high temperature. In this state, the entropy of a polymer system is maximum; as a result, the coiled state of flexible macromolecules corresponds to the minimum of free energy at sufficiently high temperature.

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* Conformations are molecular forms which convert into one another owing to free intramolecular rotation.

Chain macromolecules with a restricted rotation of units are often regarded as chains consisting of rigid regions which can undergo thermal motion independently, as it were, of one another. Such motion is usually called *micro-Brownian motion*, and the pieces of a chain which participate in it are known as *segments*. According to V. Kargin and G. Slonimsky, segmental length implies the value of a molecular weight which polymer molecules should have in order for a polymer or its solution to obey regularities that are common to low-molecular-weight substances. Thus, a segment is only an equivalent quantity which makes it possible to describe the behaviour of real polymer systems by means of well-known regularities characteristic of ideal systems.

Segmental length is often used for studying the physical properties of a polymer or of its solution. If these properties are independent of one another, segments may not coincide. For instance, segmental length calculated on the basis of viscometric data usually does not coincide with that found by osmometric measurements. Therefore, in speaking about segmental length, the property to which this quantity relates should always be indicated.

Of course, the more flexible is a molecule, the smaller should be its segment. As a rule, the segment of flexible molecules consists of 20-30 atoms of an element which constitutes the main chain. Macromolecules containing polar groups have a considerably larger segment. The dimensions of a molecule and the length of a segment coincide for very rigid molecules. Since molecular flexibility depends on temperature, segmental length should diminish as temperature rises. This length depends also on the duration of the action of an external force. Since the relaxation transition of a molecule from one conformation to another takes a definite length of time, some conformations cannot be realized in the case of rapid external effects on a molecule, and the conformation set is impoverished. As a result, a macromolecule becomes more rigid, and the segmental length, longer.

It follows that a segment, notwithstanding its conventional nature, is an indicative characteristic of chain flexibility under the given conditions.

We have considered the linear macromolecule regardless of the other molecules of a substance. But real macromolecules are always in a condensed phase, i.e., they are surrounded by other macromolecules. Therefore, in considering the behaviour of a macromolecule, account must be taken of both the interaction between atomic groups in a molecule and that between these groups and the atomic groups of adjacent molecules. Thus, the freedom of rotation about the C—C bond depends not only on the arrangement of atomic groups in a molecule, but also on the adjacent atomic groups of other molecules. In other words, owing to intermolecular interactions, the possi-

bility of a change in the shape of a chain macromolecule is determined not only by a molecule itself, but also by neighbouring molecules.

Let us now consider the connection between the flexibility of macromolecules and their chemical nature. The most flexible linear macromolecules are hydrocarbon chains because the energy barrier of free rotation is not high owing to the inconsiderable interaction between the $-CH_2-$ or $-CH_3$ groups. Among such high-molecular-weight hydrocarbons are natural rubber, polybutadiene (butadiene synthetic rubber), and polyisobutylene.*

The presence of polar substituents, e.g., —Cl, —OH, —CN and —COOH, in a macromolecule makes it less flexible because the interaction between these substituents raises the energy barrier and causes greater interaction with the polar groups of the adjacent molecules. Considerably great intermolecular forces (e.g., between chlorine atoms in polyvinyl chloride) and, under the appropriate conditions, hydrogen bonds (e.g., between carboxylic groups in polymers of acrylic acid) originate between these groups which are dipoles. All this reduces chain flexibility and increases polymer rigidity. Polymers having chains of limited flexibility (owing to the content of polar groups in them) are cellulose, polyvinyl chloride, polyacrylonitrile, and so forth.

The branching of macromolecules also strongly affects their flexibility. Short and closely arranged side chains increase macromolecular rigidity owing to a growth in the energy barrier of rotation of individual units. More spaced but longer branchings decrease intermolecular interactions and "loosen" a high-molecular-weight substance. But when the length of a side hydrocarbon chain becomes longer than the optimum, steric hindrances become more pronounced than the effect caused by a decrease in the molecular forces of attraction.

The flexibility of a macromolecule can be affected not only by the adjacent molecules of the same polymer, but also by the molecules of a solvent or a plasticizer (e.g., in solutions or plasticized polymers). In this case, a solvent between polymer molecules can cause not only a decrease in the energy barrier owing to a drop in the viscosity of a system and to the screening of the polar groups of macromolecules, but also an increase in the energy barrier as a result of the specific "adsorption" of solvent molecules on macromolecules, and this hinders free rotation about the C—C bond. In short, polymer chains can become more flexible or more rigid on dissolution, depending on the conditions.

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* The elastic properties of high-molecular-weight hydrocarbons are affected greatly by their ability to crystallize. Of course, crystallizing macromolecular hydrocarbons exhibit low elasticity and sufficiently high rigidity.

Phase states of macromolecular substances. Substances can be in three phase states: gaseous, liquid, and crystalline. The criterion of the phase state of a substance is not the outward properties, but the degree of orderliness of ions or molecules constituting the substance. The gaseous state is the most disordered phase state. In a crystalline state, a substance has the most ordered structure when a long-range order is observed, i.e., the same structural element is repeated throughout in a definite order in a crystal. The liquid state holds an intermediate position; it has a short-range order, meaning that structural elements are ordered in some regions of a liquid.

Investigation of the structure of macromolecular substances has shown that such solid substances can be either in liquid or crystalline phase states. Most high-molecular-weight substances have an amorphous liquid structure at room temperature, e.g., cellulose ethers, natural and most synthetic rubbers, and poly-*iso*-butylene. Crystalline polymers under these conditions are polyamides and polyethylene.

It was believed until recently that polymers in an amorphous state are a system of chaotically entangled macromolecules. But investigations of the last decades have shown that some structural order is observed in polymers even in an amorphous state. This order sharply grows on crystallization. According to Kargin and Slonimsky, amorphous polymeric substances, like ordinary liquids, have regions of a short-range order in which molecules are parallel to one another, forming sufficiently long bundles. The existence of such bundles does not in any way contradict high polymer elasticity because macromolecules can assume various conformations also when they form bundles. Molecules can be arranged differently in bundles which can likewise assume the most diverse shape.

Bundles in polymers can form more complex structures, even crystals and spherulites which are visible under a microscope. Thus, polymers, especially those having rigid and stereospecific molecules, often do not have the simple structure formerly ascribed to them; instead, they are very complex systems which contain both individual molecules and supermolecular structures of a different degree of complexity. Of course, both molecules and fragments of a supermolecular structure can pass over into a solution when polymers dissolve, depending on the nature of a solvent and conditions of dissolution.

4. THEORIES OF SOLUTIONS OF MACROMOLECULAR SUBSTANCES

There were two theories of polymer solutions 20-40 years ago. According to one of them, the micellar theory evolved by K. Meyer and H. Mark, macromolecules are in a solution in the form of micel-

les; according to the other, molecular theory, sufficiently diluted solutions of macromolecular substances contain individual macromolecules which are not bound to one another.

According to the micellar theory, kinetic units in a solution of high-molecular-weight substances are macromolecular bundles held together by intermolecular forces. This theory was created on the basis of the view that polymers are crystalline substances consisting of crystallites (micelles), i.e., bundles comprising 40-60 oriented macromolecules. It was believed that, on dissolution, these crystallites do not disintegrate, but continue to exist in a solution. The concepts which constituted the basis of the micellar theory were in essence the concepts of the nature of typical colloidal systems, lyosols, applied to the solutions of macromolecular substances. Both systems were believed to be heterogeneous, thermodynamically out of equilibrium, and unstable. It was held that these two types of systems differed because typical lyosols must have a stabilizer to ensure their aggregative stability whereas solutions of macromolecular substances are sufficiently stable even without a stabilizer owing to the great affinity of the dispersed phase for the dispersion medium. Therefore, solutions of macromolecular substances were formerly called "lyophilic colloidal systems".

Differences in other properties of polymer solutions and typical hydrophobic sols were attributed to high solvation. The high viscosity of polymer solutions was said to be caused by either the energetic binding of a solvent or its immobilization in polymer micelles. It was also maintained that osmotic pressure in polymer solutions grew with the concentration of a substance more rapidly than required by the linear law because the solvent in them was partially bound by a polymer and, consequently, the ratio of the number of particles of a dispersed phase to that of molecules of a free solvent increased.

But the concept of some special affinity of polymers for solvents is not substantiated well enough. As early as 1932 Marinesco determined the amount of water that was energetically bound with starch and compared the values of the dielectric constant of a solution with those of the dielectric constants of its components; he found that the amount of water was small and approximately corresponded to the formation of a monomolecular layer. A. Dumansky and S. Lipatov came to the same conclusion as a result of calorimetric investigations. Similar conclusions were drawn by A. Pasynsky who determined solvation by the compressible part of a solvent. This method is based on the fact that a solvent in a solvate shell is under great internal pressure; Pasynsky determined compressibility by the speed at which ultrasound is propagated in solutions. Generalized results of Pasynsky's investigations in the hydration of polar groups of several organic compounds are given below.

Group	—OH	—COOH	>CO	—CHO
Number of water molecules bound by the group	3	4	2	2

The results of investigations of polymer solutions in their hydrated monomers are even more convincing. In this case, it is quite senseless to speak of solvation because the forces of interaction between large and small molecules of a polymer and a monomer have the same nature and must be almost equal. However, all the phenomena characteristic of polymer solutions are observed here as well. All this refutes the notion that solvation is of some particular importance to the stability of polymer solutions, and shows that the basic principles of the micellar theory are untenable.

The micellar theory has now lost its importance. Thorough investigations have shown that macromolecular compounds in appropriate solvents are spontaneously dispersed to yield individual molecules. Typical sols and polymer solutions are similar not because micelles exist in them, but because, in both cases, rather large particles (micelles in the first case and macromolecules in the second) are contained in a solution.

The molecular theory originated almost at the same time with the micellar one. One of the authors of the molecular theory, Staudinger, believed that macromolecules existed as rigid rods in a solution. But it was subsequently shown that the behaviour of these molecules in a solution is more similar to that of flexible coiled threads.

The conformations of a coiled thread in a solution change constantly as a result of thermal motion. However, on the whole, the shape of a coil always remains similar to that of a prolate ellipsoid of revolution. This is confirmed by the fact that, whereas the length of linear macromolecules is greater than their lateral size by hundreds or thousands of times, the experimentally determined degree of asymmetry of these molecules in a solution comes to only ten.

A molecular coil is not compact when a chain is not too long, and a solvent may seep through the gaps. But as macromolecules become longer, the bent regions of a chain close the gaps and ultimately almost no solvent can pass through such a coil if the gradient of the rate of flow of a solvent is not high enough for unwinding a molecular coil into a stretched-out chain. Of course, the more rigid is a molecule, the less compact is a coil and the more is it stretched out.

Macromolecules in a solution can be in a solvated state. However, macromolecular solvation is generally not great if the medium bound in solvate terms is a solvent which interacts energetically with a polymer.

The molecular theory is confirmed by several facts and observations. First of all, a determination of molecular weights of particles in diluted polymer solutions by direct methods such as the light-

scattering method has unambiguously shown that micelles, i.e., particles consisting of molecular aggregates, are absent from such solutions.

Secondly, a macromolecular substance, like a low-molecular-weight compound, dissolves spontaneously, often evolving heat. For example, it is enough to put gelatin into water or rubber into benzene for a polymer-in-solvent solution to be formed after a certain length of time without any outside interference. In dispersing a substance up to a colloidal state, energy must be expended for overcoming intermolecular forces.

Thirdly, polymer solutions are thermodynamically stable and can be kept for an infinitely long time if the appropriate precautions are taken. Colloidal solutions are, conversely, thermodynamically unstable and are capable of aging because always, when polymers dissolve, a homogeneous system is formed and free energy decreases, just as when solutions of low-molecular-weight substances are being obtained. This happens owing either to heat evolution as a result of the polymer-solvent interaction or to an increase in entropy. But when a heterogeneous colloidal system is being obtained, its free energy always increases as the surface of a dispersed phase becomes larger.

Fourthly, for macromolecular compounds to dissolve, a stabilizer need not be present in a system. But lyophobic sols cannot be obtained without a special stabilizer which imparts aggregative stability to a system.

Lastly, polymer solutions are in thermodynamic equilibrium and are reversible systems: the Gibbs phase rule can be applied to them.

Some implications of the applicability of the phase rule to solutions of macromolecular substances were made as early as at the turn of this century. V. Kargin and his coworkers thoroughly studied such systems and established the connection between the applicability of the phase rule to the dissolution of macromolecular compounds and the thermodynamic stability and reversibility of solutions. V. Kargin, Z. Rogovin and S. Papkov studied solutions of cellulose acetate in various solvents: chloroform, dichloroethane, methanol, nitrobenzene, methyl ethyl ketone, methyl propyl ketone, benzene, toluene, and ethyl acetate. They found that, when the solubility of cellulose acetate is limited, a definite concentration of it is established in both the upper and the lower layers of a solution, depending on temperature, after a system has separated into phases and equilibrium has been attained. The dissolution process was strictly reversible and thermodynamically in equilibrium, and concentrations were the same as the preset temperature was approached by either heating or cooling. A phase diagram for the solution of cellulose acetate in chloroform is given as an example in Fig. 14.4. It is very similar to that for two finitely miscible liquids having an upper

consolute temperature. Thus, the authors came to the unambiguous conclusion that solutions of cellulose acetate obey the phase rule and are reversible systems.

The equilibrium character and reversibility of polymer solutions were proven also by V. Kargin, Z. Rogovin, A. Tager and other workers by experiments with benzyl cellulose, cellulose nitrate, polyvinyl chloride, gelatin, and other macromolecular substances. These authors obtained saturated solutions of polymers in poor solvents in various ways. If equilibrium (the separation of a solution into two phases or the attainment of maximum dissolution) was reached at the same temperature and pressure, solutions had always the same concentration. Phase diagrams with an upper consolute temperature were plotted for the above-mentioned macromolecular substances. But there are data to the effect that diagrams with a lower consolute temperature are obtained for aqueous solutions of methyl cellulose and ethyl cellulose.

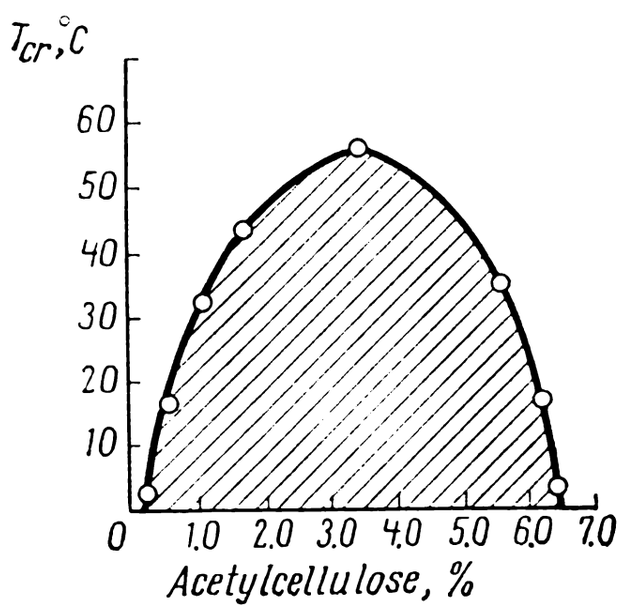

Fig. 14.4. Phase diagram for the solution of cellulose acetate in chloroform

Therefore, the phase rule, inapplicable to colloidal systems, is obeyed when both macromolecular and low-molecular-weight substances dissolve. Indeed, it may take a long time (for example, several months) to establish equilibrium in polymer solutions because of their very high viscosity, and the chemist often has to work with non-equilibrium systems. But this does not change the gist of the matter.

Polymer molecules are not bound to one another and behave quite independently only when they are in relatively diluted solutions. In concentrated solutions, when collisions between molecules of a solute are quite probable, macromolecules can interact and form clusters, or associates. These associates consist of a rather small number of molecules and represent a prototype of bundles already mentioned in our consideration of the polymer structure. They are usually not large enough and therefore cannot be regarded as a phase. Unlike micelles, associates do not exist permanently; they originate in one place, then disintegrate and originate again in another. Thus, associates in diluted polymer solutions are not permanent formations and do not have a definite composition.

The formation of associates is characteristic of not only solutions of macromolecular substances. Associates are formed also in solu-

tions of low-molecular-weight substances and in individual liquids when two or more molecules collide with or cohere to one another. Consequently, association is similar to the fluctuation of densities in solutions and in individual liquids. Association in solutions of macromolecular substances is characterized by the fact that regions of long and flexible macromolecules can be in the composition of various associates.

Macromolecules are bound in an associate like molecules in associates which originate in low-molecular-weight systems: by intermolecular interactions, by hydrogen bonds and, in aqueous solutions, by electrostatic forces. The forces which prevail in the formation of associates must be determined in every individual case, and the nature of a solvent must be taken into account. For example, in water, interaction involves mainly the hydrocarbon parts of molecules, and in a hydrocarbon medium, polar groups.

Association is strongly affected by temperature. As temperature rises, the thermal motion of associates increases, and this causes their destruction. Conversely, a drop in temperature promotes the association.

The average lifetime of associates in the solutions of low-molecular-weight substances is very short, being about 10^{-10} second. It is considerably longer in solutions of macromolecular substances because much more time is needed for bulky macromolecules to tear away from one another. The formation and destruction of associates with a change in temperature or concentration are reversible, i.e., the average statistical dimensions of associates in a solution of macromolecular substances are quite definite under preset conditions. But since the lifetime of associates consisting of macromolecules is longer, the equilibrium value of the degree of association in solutions of macromolecular substances is not established immediately.

The dimensions and lifetime of macromolecular associates increase with a growth in the concentration of their solutions or a drop in temperature. As a result, under definite conditions, associates may become so large and stable that they can be regarded as a new phase. In the formation of this second phase, a system acquires the ability to separate into phases; for example, in coacervation, a newly formed phase separates as minute droplets.

Since macromolecules are considerably long and flexible and can be in the composition of several associates, association in solutions can ultimately cause the formation of a three-dimensional network in a system which becomes a gel. The presence of such networks, which impart elastic properties even to rather diluted polymer solutions, was proven by Freundlich and Seifriz as early as at the turn of this century. Using a microscope, they established that if a magnetic field acts on a minute nickel grain even in a very viscous liquid, the grain can move in the liquid by any great distance. But in

solutions of macromolecular substances, the grain moves in the magnetic field by a very short distance and then stops; in the absence of the field, the grain returns to its initial position under the action of elastic forces engendered by the existence of a macromolecular network in a solution. A gelated solution undergoes syneresis in the course of time, separating into two phases: a solution of a macromolecular substance in a solvent and a solution of a solvent in a macromolecular component. It follows that associates are nuclei of a new phase.

Besides solutions of polymers, their dispersions can also exist, and they possess all the properties of colloidal systems (see Chap. 14, Sec. 8). Particles of such dispersions are large macromolecular aggregates.

5. THERMODYNAMICS OF DISSOLUTION OF MACROMOLECULAR SUBSTANCES

The dissolution of macromolecular substances is usually regarded as the mixing of two liquids. This viewpoint takes account of (a) the energy interaction between the molecules of a substance being dissolved and of a solvent and (b) the entropy factor which causes the uniform distribution of solute molecules in a solution. The similarity between the dissolution of a macromolecular substance and the mixing of two liquids is not merely formal, but corresponds to the very essence of the phenomenon. For example, the limited swelling of a macromolecular substance corresponds to the limited mixing, whereas unlimited swelling, which becomes dissolution, to the unlimited mixing.

The spontaneous dissolution of a macromolecular compound or any other substance must be accompanied at constant pressure by a decrease in Gibbs free energy.

According to the second law of thermodynamics, a change in the Gibbs free energy of a system is

$$\Delta G = \Delta H - T\Delta S \qquad (14.3)$$

where H = enthalpy;
T = absolute temperature;
S = entropy.

When a system does not change its volume, and this can be accepted as a certain approximation for the dissolution process, Eq. (14.3) can be substituted by

$$\Delta F = \Delta U - T\Delta S \qquad (14.4)$$

where F = Helmholtz free energy;
U = internal energy.

Apparently, for a polymer to dissolve spontaneously, ΔG or ΔF must have a negative value, and they have it in two following cases.

1. When $\Delta H < 0$ (or $\Delta U < 0$) which is observed if heat is evolved on dissolution because a change in enthalpy (or internal energy) is equal to the integral heat of dissolution with an opposite sign. Such a condition is often met in practice, e.g., when polar polymers are dissolved in polar solvents. The thermal effect is positive on dissolution because the heat of solvation of macromolecules is greater than that of dissolution proper, and the total heat effect of dissolution is equal to the algebraic sum of the heats of solvation and of dissolution proper.

2. When $\Delta S > 0$ which is always realized in practice on dissolution because the entropy of mixing is always positive. The entropy of mixing of a macromolecular substance with a solvent, calculated per weight fraction of a substance, is between the entropy of dissolution of low-molecular-weight substances and that of typical colloidal systems. Therefore, the entropy factor plays a smaller role in the dissolution of macromolecular compounds than in the dissolution of low-molecular-weight ones, and the energy factor (solvation) is of greater importance. However, since the entropy term is not equal to zero, but can have a rather high value, some polymers can dissolve with heat absorption, and not with heat evolution, i.e., when $\Delta H > 0$ (or $\Delta U > 0$). This is because, in such cases, $T\Delta S > > \Delta H$ (or $T\Delta S > \Delta U$) and consequently ΔG (or ΔF) is less than zero.

The molar entropy of mixing of two substances for an ideal system, or a change in the entropy of a system when a certain amount of a substance dissolves in a given solvent volume, is found from the thermodynamic equation

$$\Delta S_{id} = -R\,(n_1 \ln N_1 + n_2 \ln N_2) \tag{14.5}$$

where R = universal gas constant;
n_1 and n_2 = number of moles of the components being mixed together;
N_1 and N_2 = molar fractions of both components.

In this equation, the subscripts 1 and 2 denote quantities which relate to the solvent and the solute, respectively.

Partial molar entropies of mixing can be calculated by the equations

$$\Delta \bar{S}_{1,\,id} = \partial \Delta S / \partial N_1 = -R \ln N_1 \tag{14.6}$$

and

$$\Delta \bar{S}_{2,\,id} = \partial \Delta S / \partial N_2 = -R \ln N_2 \tag{14.7}$$

If we proceed from concepts used in calculating the ideal entropy of mixing of isodiametric molecules, which depends only on the number of the molecules being mixed together, an increase in the molecular weight of one component should cause a decrease in the number of molecules of the component in one gram of a system and consequently a diminution in the entropy of mixing of the given amounts of weight of both substances. Enthalpy (or internal energy) should not change because the amounts of weight of the components being mixed together and consequently the number of interacting atomic groups do not change. It follows that, as the molecular weight of a polymer increases, the role of the entropy term $T\Delta S$ in Eqs. (14.3) and (14.4) will permanently decrease and the energy term ΔH or ΔU should become determinative.

However, when the dissolution of macromolecular substances having chain molecules was being studied, such a dependence was found only for polymers having rigid molecules.* But when flexible chain molecules dissolve in low-molecular-weight liquids, the entropy of mixing is usually much higher than that of mixing of an ideal system, and it is the greater, the larger is the molecular weight of a polymer. The unusually high entropy of mixing when polymers dissolve, being hundreds and thousands of times higher than the ideal one, is said to be due to the fact that segments of flexible chain molecules can then easier move in a solution. It can be assumed that macromolecular segments act as individual kinetic units in a solution. In other words, polymers having flexible molecules act as if they possessed the ideal entropy of mixing but had a smaller molecular weight (the amount of weight being the same).

According to statistical physics, entropy increases in the dissolution of macromolecular substances because macromolecules in a solution can be arranged differently, and each macromolecule can realize a large number of conformations. In an undissolved polymer, chain molecules hinder one another from assuming different conformations. When small molecules of a solvent are present between macromolecules, the constraining action of molecular chains on one another becomes less; macromolecules can assume almost any conformation in a maximally diluted solution when they are very far away from one another. In other words, the thermodynamic probability of state of macromolecules in a low-viscous solution is greater than in the initial polymer.

Let W_i stand for the initial thermodynamic probability of state of macromolecules (before dissolution) and W_f, for the final one

* The entropy of mixing will be higher than the ideal one even when substances having rigid, stretched-out molecules are dissolved in a low-molecular-weight liquid having isodiametric molecules because the number of arrangements of such stretched-out molecules is ar greater than that of the arrangements of the same number of isodiametric molecules of both kinds.

(after dissolution). Probability W is connected with entropy S by the Boltzmann equation

$$S = k \ln W \tag{14.8}$$

where k is the Boltzmann constant.

A change in entropy when a substance passes into solution will then be

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln (W_f/W_i) \tag{14.9}$$

Since the probability of W_f is always greater than that of W_i, an increment in the entropy of dissolution is always positive. It follows from the equation that the entropy of a system always grows with an increase in probability as a result of dissolution.

An important conclusion which can be drawn from the foregoing is that macromolecular substances having flexible macromolecules should dissolve better than those having rigid ones because the former can be arranged in a solution in a considerably larger number of ways. Moreover, for rigid macromolecules which are usually parallel to one another, the energy of interaction between molecular chains is very high, and it is very difficult to tear them away from one another. That is why there is a limited number of solvents for macromolecular substances having rigid chains, such as cellulose, polyvinyl chloride, or polyamides.

It is important to meet one condition for dissolution: a decrease in the Gibbs free energy of a system. Therefore, dissolution can be realized also when the thermal effect is negative, but the entropy of a system grows so much on dissolution that it ultimately causes a diminution in the Gibbs free energy.

As temperature rises, the value of the entropy factor increases; therefore, any macromolecular substance and any solvent should have consolute temperature T_{con} above which they mix together at any ratio. Theoretically, such consolute temperature should exist for any combination of a macromolecular substance and a solvent. But, in practice, it cannot be attained in many cases owing to the low boiling point of a solvent and the low temperature of destruction of a macromolecular substance. Consolute temperature can easily be found from the condition $\Delta H - T_{con}\Delta S = 0$ or $\Delta H = T_{con}\Delta S$.

Whence

$$T_{con} = \Delta H/\Delta S \tag{14.10}$$

where ΔH and ΔS are changes in enthalpy and entropy in dissolution, respectively.

Recent experiments have shown that, when polymers dissolve, the entropy factor is cardinal in some cases due to the unusually great entropy of mixing. For example, it almost wholly determines the

solubility of non-polar polymers in hydrocarbons. Therefore, Katz and Brönsted who tried to attribute polymer solubility only to the effect of the energy factor turned out to be wrong. But when polar polymers are involved, e.g., when gelatin is dissolved in water or cellulose nitrate is dissolved in acetone, the energy factor can be of considerable importance and its effect must not be ignored.

Let us consider the causes of polymer dissolution by taking some typical examples. To this end, let us use Table 14.1 compiled by A. Pasynsky.

Table 14.1. **Relationship Between Thermodynamic Quantities in the Dissolution of Macromolecular Compounds**

System	Character of dissolution	ΔH	ΔS	ΔG
Cellulose nitrate in cyclohexanone	Exothermal	<0	$\geqslant 0$	<0
Egg albumin in water	Ditto	<0	<0	<0 (at $\Delta H > T\Delta S$)
Poly-*iso*-butylene in *iso*-octane	Isothermal	0	>0	<0
Rubber in toluene	Endothermal	>0	>0	<0 (at $\Delta H < T\Delta S$)

Data in Table 14.1 show that polar cellulose nitrate dissolves in polar cyclohexanone as a result of both a decrease in enthalpy ($\Delta H < <0$) and an increase in entropy ($\Delta S > 0$). Since both factors promote mixing, cyclohexanone is a good solvent of cellulose nitrate.

When a polar egg albumin is dissolved in water (a polar solvent), the process occurs at first only because of a decrease in enthalpy. Entropy increment at the initial stage even has negative values owing to great polymer hydration. (Water molecules in a hydrate shell become more ordered, and polymer molecules may become less flexible when they are hydrated.) But for a polymer to dissolve, the absolute value of ΔH must be greater than $T\Delta S$. However, in the course of hydration, hydrated polymer molecules dissolve in excess water with ever smaller heat evolution. Dissolution at this final stage occurs mainly because molecules can be distributed throughout the volume of a system, i.e., it occurs due to the entropy factor.

Non-polar poly-*iso*-butylene dissolves in non-polar *iso*-octane only as a result of an increase in entropy without heat evolution, i.e., mixing is of an isothermal character in this case. When poly-*iso*-butylene dissolves in *iso*-octane, a hydrated dimer of *iso*-butylene, the energy barrier does not change as units of a molecular chain revolve because the action of intermolecular forces in a solution is of the same

nature as in poly-*iso*-butylene. In other words, dissolution occurs here without a change in macromolecular flexibility.

Rubber dissolves in toluene also owing to an increase in the entropy of mixing. This case differs from the preceding one by the fact that a small negative thermal effect is observed. But this effect is more than compensated by an increase in entropy because rubber molecules are very flexible.

The combinations concerning a change in enthalpy and entropy given in Table 14.1 cover all the typical cases of polymer dissolution. Dissolution does not occur in other combinations of these quantities because then $\Delta G > 0$.

6. SWELLING OF MACROMOLECULAR SUBSTANCES

The dissolution of macromolecular substances having linear flexible molecules, unlike that of low-molecular compounds, is accompanied by swelling; to be more exact, the swelling of such substances is the first stage of their dissolution. In swelling, a macromolecular substance absorbs a low-molecular-weight solvent, considerably increases in mass, and changes its mechanical properties without losing homogeneity. The volume of a macromolecular substance can increase on swelling by as much as 1000-1500 per cent.*

Swelling is of great importance in nature and technological processes. It is the basis of such processes as the gelation of starch, mercerization in textile technology, and the fat-liquoring of a depilated hide in the tanning industry. Several phenomena in animal and plant organisms can also be attributed to swelling.

Swelling occurs on dissolution not only because molecules of a substance being dissolved diffuse into a solvent, as is the case with the dissolution of low-molecular-weight substances, but mainly because molecules of a solvent diffuse into a macromolecular substance. The latter occurs because macromolecules are packed rather loosely in ordinary amorphous macromolecular substances; as a result of the thermal motion of flexible chains, very small gaps into which solvent molecules can penetrate are regularly formed between the chains. Since small solvent molecules are far more mobile than macromolecules, the former at first mainly diffuse into a polymer, causing an increase in its volume; only later do macromolecules, the bonds between which have been greatly weakened, tear away from the main mass of a substance and diffuse into a medium, forming a homogeneous true solution.

Since solubility is connected with the motion of not the entire macromolecule but of its segments in a solution, solubility does

* Swelling must not be confused with capillary imbibition when a liquid fills microscopic voids in a solid whose dimensions usually do not increase.

not depend on the molecular weight of a polymer. However, this weight considerably affects the dissolution rate. The lower is the molecular weight, the more does the dissolution of a polymer resemble that of a low-molecular-weight substance. For example, destroyed rubber dissolves without swelling. Conversely, polymers dissolve more slowly as the molecular weight increases. At very low dissolution rates, which are observed when polymer molecules are very large, one may even erroneously believe that a substance is insoluble. If polymer molecules are rigid, i.e., if segmental length is almost equal to the length of the entire chain, solubility must depend on the extent of polymerization.

Macromolecular substances having spherical molecules either do not swell at all or swell very poorly on dissolution. A typical example is glycogen which consists of globular molecules whose weight is as high as 800,000. Glycogen does not swell on dissolution, indicating that diffusion cannot be regarded as the sole factor which controls swelling. Substances having spherical macromolecules are incapable of swelling because the cohesive forces acting on a spherical molecule are always less than the forces acting on a linear macromolecule since a spherical macromolecule has a relatively small contact area. The low cohesive energy of macromolecular substances having spherical molecules facilitates their dissolution.

Such swelling of macromolecular compounds having linear molecules is observed in the simplest case when swelling and dissolution are almost of a purely entropy nature, such as the dissolution of rubbers in hydrocarbons. The dissolution mechanism becomes more complicated when solvent molecules energetically interact with molecules of a macromolecular substance, for example, when gelatin dissolves in water. In this case, it can be assumed that dissolution goes through two stages although the second stage begins in fact before the first one ends.

At the first stage of swelling, macromolecules solvate as a solvent diffuses into a macromolecular substance. This stage is characterized by heat evolution and the ordered arrangement of solvent molecules near macromolecules; therefore, the entropy of a system even decreases at the first stage of dissolution. At this stage of dissolution, the bonds between macromolecules are destroyed, and chains thus become free and capable of undergoing thermal motion.

The second stage is swelling or dissolution caused by purely entropy factors. At this stage, when solvation is already completed, the thermal effect is equal to zero or even has a negative value whereas entropy increases sharply because bulky and flexible macromolecules mix together with small solvent molecules. The second stage of dissolution can be regarded as a purely osmotic process.

The physical state of polymers affects their swelling and dissolution. Of course, polymers in the viscofluid and viscoelastic states

swell and dissolve most readily, as their molecules are bound to one another least strongly. Polymers in a glassy state dissolve with considerably greater difficulty. In this case, when a polymer comes into contact with a solvent, solvent molecules penetrate into the surface layer of the polymer, and this causes its surface swelling. The swollen polymer then dissolves in the same way as a high-elastic polymer. The interface between a solid polymer into which the solvent still has not penetrated and its swollen layer gradually moves into a substance at the rate of diffusion of a solvent into a glassy polymer.

The most sparingly soluble polymers are crystalline ones. The disordered regions of such polymers will be the first to react with a solvent. A solvent will be able to penetrate into crystalline regions if it exothermally reacts with a polymer because the destruction of crystalline regions is always accompanied by considerable heat absorption. Otherwise, the crystalline part of a system must be heated in order to dissolve it.

It is far from always that swelling ends with dissolution. The process stops very often after a certain degree of swelling is attained. A cause of such a phenomenon is that a macromolecular substance and a solvent are capable of mixing to a limited extent. Therefore, two phases are formed in a system as a result of swelling; a saturated polymer-in-solvent solution (solution proper) and a saturated solvent-in-polymer solution (gel, jelly). Such limited swelling is of an equilibrium nature, i.e., the volume of a maximally swollen macromolecular substance remains unchanged infinitely long, provided chemical changes do not occur in a system. Examples of swelling caused by limited dissolution are the swelling of polyvinyl chloride in acetone and that of polychloroprene in benzene. Limited swelling, caused by limited dissolution, often becomes unlimited swelling when experimental conditions are changed. For instance, gelatin and agar, which swell to a limited extent in cold water, swell to an unlimited extent in warm water.

At present, it is still impossible to exactly establish the connection between the nature of a solvent and its ability to dissolve a given macromolecular substance, and one usually confines oneself to the empirical rule of like dissolves like. In other words, non-polar polymers dissolve in non-polar solvents, and polar polymers dissolve in polar solvents. G. Gee established the relationship between the ability of solvents to cause the swelling and dissolution of a polymer, and the values of the densities of cohesive energies of the solvents. The specific density of cohesive energy E/V_{mol} (where E is cohesive energy or latent heat of evaporation, and V_{mol} is the molar volume) is energy which must be expended in order to draw apart molecules contained in 1 cm^3 of a polymer by a distance transcending the sphere of their action. Several examples were taken to show that maximum swelling is observed when the specific densities of

the cohesive energy of a solvent and that of a polymer are either equal or similar to one another.

Another cause of limited swelling of a macromolecular substance is that chemical cross-links (so-called bridges) may exist between polymer molecules, and the substance is a three-dimensional network. This prevents macromolecules from tearing away from one another and passing over into a solution. Even if not all the polymer molecules are bound into a three-dimensional network, such a network may act as a membrane which is permeable for small solvent molecules and which hinders the diffusion of macromolecules from the volume of a swollen polymer. As the volume of a macromolecular substance increases on swelling, stresses originate in the network, and this terminates swelling. An example of limited swelling, caused by the presence of a strong three-dimensional network, is the swelling of vulcanized rubber in benzene.

The limited dissolution of a polymer as a result of the presence of a three-dimensional molecular network in it can be interpreted also in thermodynamical terms. Indeed, when such a polymer swells, the flexible regions of macromolecules which are between network nodes become elongated and straighten out; consequently, the "entropy springs" are now in a less probable state. As a result, the entropy of a system decreases; this decrease may become equal to an increase in entropy as a result of mixing. At this moment, swelling ceases, i.e., the system reaches an equilibrium state. These considerations are confirmed by the relationship between the elasticity modulus of polymers and their ability to swell studied by P. Flory.

When there is a large number of chemical cross-links between macromolecules, a polymer ceases not only to dissolve, but also to swell. An example is ebonite which is vulcanized rubber having a sulphur content of 25-30 per cent. The density and rigidity of the three-dimensional network prevent solvent molecules from penetrating into the polymer and drawing apart its chains. Therefore, ebonite does not swell. When there is a small number of bonds between macromolecules, a polymer which swells to a limited extent can be converted into a polymer which swells to an unlimited extent by means of mechanical treatment, such as rolling. In rolling, sparse cross-links are ruptured, and a polymer acquires the ability to dissolve.

There is no basic difference between both possible cases of limited swelling, one of which is engendered by limited mixing, and the other, by the three-dimensional polymer structure. It can be taken that, in the first case, the polymer also has such a network, but the bonds are of intermolecular instead of chemical nature. The limited dissolution of a polymer can then be attributed to the fact that a poor solvent either cannot destroy these bonds or cleaves them only partially, and this is expressed in limited swelling.

There is a third explanation to the limited swelling of polymers, proposed by Kargin. Suppose that macromolecules become less flexible as a result of solvation on swelling or dissolution. This can be caused by an increase in the potential barrier of rotation of molecular regions owing to interaction with a solvent. The entropy of a polymer will then diminish on swelling because macromolecules become increasingly rigid and cannot realize the conformations which they could assume when a solvent was absent. Swelling ends as soon as a decrease in entropy owing to the loss in macromolecular flexibility becomes greater than the diminution of internal energy as a result of the energetic interaction between macromolecules and solvent molecules, i.e., as soon as the Gibbs free energy of a system ceases to decrease. This occurs, for example, when cellulose acetate swells in tetrachloroethane or when polar macromolecular substances swell in water. Table 14.2 gives the partial values of $\Delta\bar{H}_1$, $\Delta\bar{G}_1$ and $T\Delta\bar{S}_1$ of water in agar, casein, keratin, and cellulose that are swollen to a different extent. According to Kargin and Tager, the potential barrier of rotation sharply grows as a result of interaction between solvent molecules and macromolecules when all the above-mentioned substances swell; this causes a decrease in entropy and an increase in the free energy of a system. Consequently, swelling ends at a definite stage and dissolution does not occur.

Table 14.2. **Partial Thermodynamic Characteristics of Water (in cal/mol) in Some Swollen Polymers**

Polymer	t, °C	$\Delta\bar{H}_1$	$\Delta\bar{G}_1$	$T\Delta\bar{S}_1$	$\Delta\bar{H}_1$	$\Delta\bar{G}_1$	$T\Delta\bar{S}_1$
		(5.7 per cent of H_2O, 0.943 molar fractions of a substance)			(10.8 per cent of H_2O, 0.892 molar fractions of a substance)		
Agar	5	—3200	—1850	—1350	—1850	—1000	—850
Casein	5	—2050	—900	—1150	—1000	—350	—650
Keratin	5	—2250	—1200	—1050	—1150	—500	—950
Ditto	20	—2800	—1100	—1400	—1650	—450	—1200
Cellulose	50	—1000	—230	—770	—200	—30	—175

The swelling of a polymer in a liquid is characterized by the degree of swelling α which is calculated by the equation

$$\alpha = (m - m_0)/m_0 \qquad (14.10)$$

where m_0 and m are masses of samples before and after swelling.

Apparently, the degree of swelling is numerically equal to the mass (in grams) of a liquid absorbed by 1 g of a polymer. In determining α, it should be taken into account that low-molecular-weight

fractions are washed out from a polymer in the course of swelling; therefore the degree of swelling calculated by Eq. (14.10) may be somewhat lower than that in solvent vapours.

In determining the degree of swelling at definite intervals, curves characterizing the kinetics of swelling can be plotted. Swelling is often determined not by a gain in weight, but by an increase in the volume of a specimen. Fig. 14.5 shows the typical kinetic curves of swelling. Curves *2* and *3* characterize limited swelling: curve *2* corresponds to rather rapid swelling of a polymer but with a low

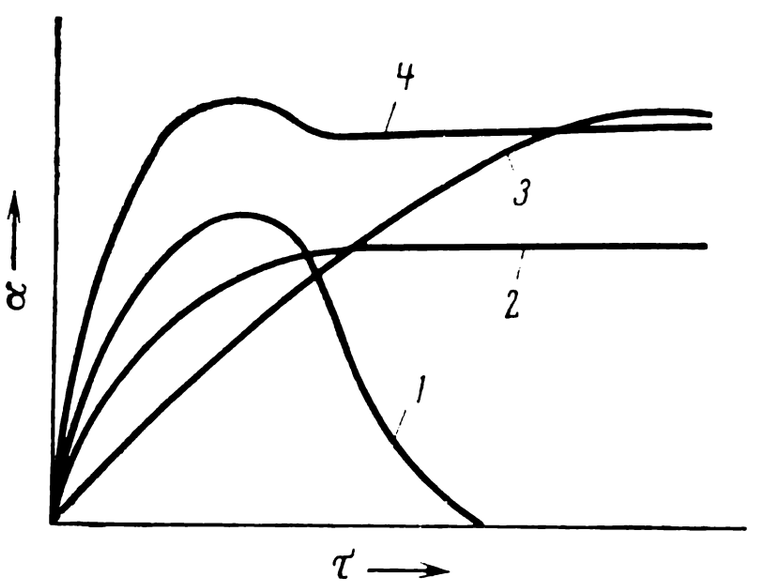

Fig. 14.5. Kinetic curves of swelling:
1—unlimited swelling; *2*—rapid swelling with a low limit of swelling; *3*—slow swelling with a high limit of swelling; *4*—limited swelling with the extraction of low-molecular-weight fractions

limit of swelling; curve *3* stands for a slowly swelling polymer having a high limit of swelling. Both curves rise steeply at the beginning, and then they smoothly become a straight line which is parallel to the abscissa. Analytically, these curves can be represented by the differential equation

$$d\alpha/d\tau = k\,(\alpha_{max} - \alpha_\tau) \qquad (14.11)$$

where α_{max} = maximum degree of swelling;
α_τ = degree of swelling at moment τ;
k = swelling rate constant which depends on the nature of a polymer and that of a solvent, and on temperature.

As a result of integration, the equation becomes

$$k = \frac{1}{\tau} \ln \frac{\alpha_{max}}{\alpha_{max} - \alpha_\tau} \qquad (14.12)$$

The rates of swelling of various polymers should be compared by the slope of the tangents plotted to the curves from the coordinate origin, and the ability of polymers to swell should be characterized by the greatest extent of swelling.

Curve *1* (Fig. 14.5) characterizes unlimited swelling when a polymer dissolves in a solvent. In this case, we cannot speak of the greatest degree of swelling although the curve has a maximum. Curve *4* characterizes limited swelling when a considerable amount of low-molecular-weight fractions are extracted from a swelling substance, and this reduces the maximum degree of swelling.

The shape of a sample can greatly affect swelling. Therefore, experiments in which the swelling of various polymers is compared must always be carried out with samples of the same shape.

When a macromolecular substance swells, considerably high pressure may originate if something prevents the volume of a sample from increasing. For example, when wood swells in water, pressure may reach tens of atmospheres. This pressure is so high that the phenomenon was used in ancient times to split up cliffs: wooden wedges were driven into cracks in cliffs and then the cracks were filled with water; the wedges swelled in water, tended to increase their dimensions, and thus created pressure which broke up a cliff.

Pressure p, which develops in swelling, can be calculated by Posnjak's equation:

$$p = p_0 c^k \tag{14.13}$$

where p_0 = constant which depends on the nature of a polymer and of a solvent, and on temperature;
c = content of a dry polymer in a swelling gel;
k = constant whose value usually approximates 3.

Apparently, at $c = 1$, p should be equal to p_0. When the logarithm of the equation is taken, it becomes

$$\ln p = \ln p_0 + k \ln c \tag{14.14}$$

This straight-line equation makes it possible to find graphically the quantities p_0 and k, and p can also be determined when the constants are known and at a given value of c.

Figure 14.6 shows an example of the logarithmic dependence of pressure on concentration for rubber which swells in various solvents. As we may see, the relationship between $\ln p$ and $\ln c$ is of a linear nature and the constant remains the same for all the tested solvents. If the liquids in which rubber swelled are arranged in the order of an increase in constant p_0, they would form the same series as that where they are in the order of an increase in the maximum degree of swelling. This indicates a relationship between swelling pressure and the maximum degree of swelling.

Besides an increase in the volume of a macromolecular substance, swelling is often accompanied at the beginning with a decrease in the volume of the system and with the thermal swelling effect. These phenomena are very important in understanding the mechanism of swelling.

On swelling, the polymer volume always increases while the volume of the system (polymer + solvent) usually decreases. This is especially noticeable when polar polymers swell in polar solvents. A diminution in the volume of a system on swelling, known as *contraction*, is in most cases described by the empirical equation

$$V = \alpha m/(\beta + m) \quad (14.15)$$

where V = contraction;
m = mass of a liquid imbibed when 1 g of a polymer swells (degree of soaking);
α and β = constants.

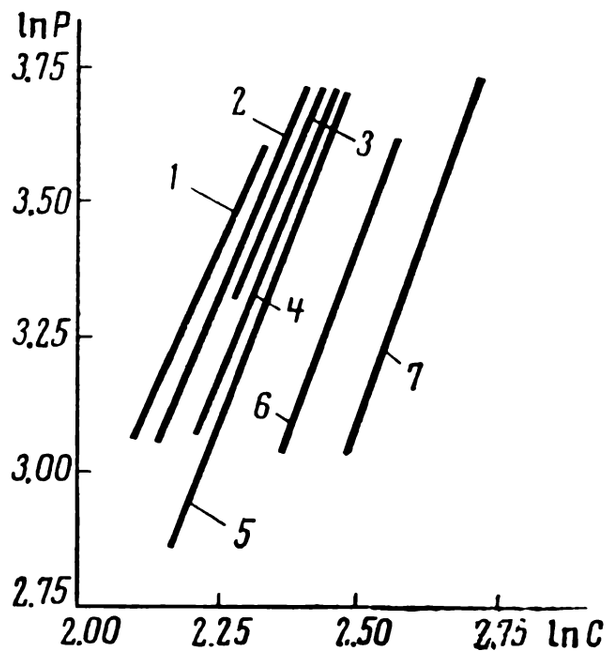

Fig. 14.6. Dependence of ln p on ln c in the case of swelling of natural rubber in various solvents:
1—carbon tetrachloride; *2*—chloroform; *3*—tetrachloroethane; *4*—toluene; *5*—benzene; *6*—diethyl ether; *7*—dichloroethane

A system contracts as a polymer swells because solvent molecules become oriented as a result of their "adsorption" by macromolecules, and this increases the density of a system. In addition, contraction partially occurs owing purely to the steric factor; on swelling, small solvent molecules penetrate into gaps between bulky macromolecules, so that molecular packing becomes more compact.

The thermal effect is usually positive when a macromolecular substance swells, e.g., when polar polymers swell in polar solvents. This is quite clear because heat is evolved on swelling upon the interaction between polymer molecules and solvent molecules. The integral heat of swelling q_{int} is the total amount of heat evolved when 1 g of a dry polymer swells; the differential heat of swelling q_{dif} is the amount of heat evolved when 1 g of a liquid is imbibed by either a dry or a swollen polymer.

Table 14.3 gives an example of the integral and differential heats of swelling of some macromolecular substances (according to Katz and Mark).

The integral heat of swelling q_{int} consists of three quantities: q'_{int} which is heat that corresponds to work required for separating macromolecules; q''_{int} which is heat that corresponds to work required for separating solvent molecules; and q'''_{int} which is heat that is evolved upon the interaction between a solvent and a polymer. The first two quantities are always negative, and the third is positive:

$$q_{int} = -q'_{int} - q''_{int} + q'''_{int} \quad (14.16)$$

Table 14.3. **Integral and Differential Heats of Swelling (in cal/g) of Some Macromolecular Substances**

Macromolecular substance	Solvent	q_{int}	q_{dif} (for a dry substance)
Casein	Water	25.4	265
Nuclein	Ditto	23.4	310
Induline	Ditto	21.8	420
Wood fibre	Ditto	16.9	—
Cellulose	Ditto	10.7	390
Cellulose acetate	Trichloroethylene	11.4	108
Ditto	Benzyl chloride	8.1	76
Ditto	Benzyl alcohol	8.2	69
Cellulose nitrate	Formic acid	6.8	60
Ditto	Ethyl alcohol	5.5	87

When a non-polar macromolecular substance swells in a non-polar liquid, the absolute values of q'_{int}, q''_{int} and q'''_{int} are similar to one another and are not high; therefore, the thermal effect approximates zero. When a polar macromolecular substance swells in a polar solvent, the value of q'''_{int} is as a rule high and dissolution is accompanied by heat evolution. For crystalline polymers, the value of q'_{int} is usually high. In this case, the heat of swelling may be negative, making swelling difficult.

The differential heat of swelling is the lower, the higher is the degree of swelling of a macromolecular substance. As an example, let us take the differential heats of swelling of gelatin which were found by interpolation:

Mass of water imbibed by 1 g of gelatin, g	0.000	0.005	0.041	0.103	0.242
q_{dif}, cal/g	228	222	186	142	86

As we may see, the differential heat of swelling rapidly drops as a polymer substance becomes soaked to a greater extent. When soaking is considerably high, the thermal effect of swelling can equal zero or even assume a negative value.

The integral heat of swelling q_{int} can be represented by an equation similar to that for contraction:

$$q_{int} = ai/(b+i) \qquad (14.17)$$

where i = degree of soaking;
a and b = constants.

The ratio of contraction to the integral heat of swelling is as a rule a constant, i.e.,

$$V/q_{int} = \text{const} \tag{14.18}$$

Thus, contraction and heat evolution on swelling are usually interconnected processes which occur mainly as a result of the interaction between molecules of a macromolecular substance and solvent molecules that have diffused into it, i.e., they occur as a result of solvation.

Eqs. (14.15) and (14.17) are similar to Langmuir's adsorption equation (4.10). This is additional proof that solvation has the adsorption nature.

Let us consider now the effect of temperature on limited swelling.

The effect of temperature on swelling can be easily determined by considering a process in thermodynamical terms. If swelling is an exothermal process which is characteristic of its first stage, the equilibrium degree of swelling decreases with an elevation of temperature. For example, the limited swelling of cellulose in water or in a solution of sodium hydroxide is a typical exothermal process, and it greatly decreases with an elevation of temperature. However, swelling can become an endothermal process at the second stage and then it should increase with an elevation of temperature, as does in fact gelatin swelling. The rate of swelling should always grow with an elevation of temperature which accelerates the establishment of an equilibrium state of a system.

The effect of electrolytes on polymer swelling is considered below in Sec. 8 when the properties of the solutions of macromolecular electrolytes are described because polyelectrolytes exhibit this effect most powerfully.

7. SOME PROPERTIES OF SOLUTIONS OF MACROMOLECULAR SUBSTANCES

Raoult's law and apparent molecular weight of polymers. Ideal solutions, i.e., solutions which are formed without a change in enthalpy and whose entropy is equal to that of mixing of ideal solutions, obey Raoult's law. This law determines several important properties of solutions, depending on their content of a solute. If a solute is non-volatile, i.e., if the pressure of its vapours is practically zero, Raoult's law can be expressed as

$$p_1/p_1^0 = N_1 = 1 - N_2 \tag{14.19}$$

where p_1 = pressure of solvent vapours above a solution;
p_1^0 = pressure of vapours above a pure solvent;
N_1 and N_2 = molar fractions of a solvent and a solute in a solution, respectively.

Raoult's law is often inapplicable to real solutions, and two types of deviations are observed: (1) negative deviation when the ratio p_1/p_1^0 is less than the molar fraction of a volatile component in a solution (i.e., $p_1/p_1^0 < N_1$), and (2) positive deviation when the ratio p_1/p_1^0 is greater than the molar fraction of a solvent in a solution (i.e., $p_1/p_1^0 > N_1$).

Fig. 14.7 shows the dependence of p_1/p_1^0 on the molar fraction of solute N_2 for an ideal solution and for real solutions having negative and positive deviations from Raoult's law.

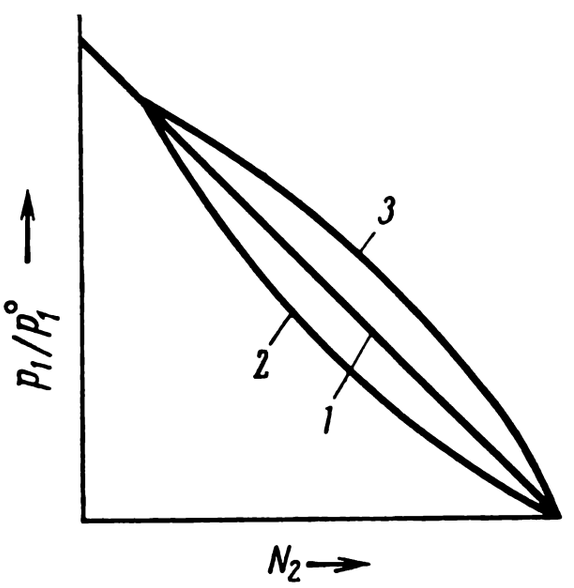

Fig. 14.7. Dependence of p_1/p_1^0 on N_2 for an ideal solution (*1*), for real solutions with a negative deviation from Raoult's law (*2*), and for real solutions with a positive deviation from it (*3*)

For a long time, the deviation in the behaviour of real solutions from Raoult's law was attributed only to the energetic interaction between solvent molecules and solute molecules. Negative deviations were said to be due to the stronger retention of solvent molecules by non-volatile molecules of a solute than by the same kind of molecules. Such a strong interaction indicates the affinity between a solvent and a solute; therefore, negative deviations must always be observed when both components are highly compatible and also in solvation and when additive compounds are formed. In the case of negative deviations due to the same causes, a system contracts and heat is evolved.

Positive deviations were attributed to the stronger interaction between molecules of the same kind than between those of a different nature. This causes solvent molecules to be forced out of a solution and, consequently, the pressure of its vapour above the solution will be higher than it should be according to Raoult's law. Positive deviations indicate the poor compatibility of the two components. It is therefore clear that heat is always absorbed and the volume of a system increases in positive deviations.

However, as further investigations have shown, deviations in the behaviour of real solutions from Raoult's law can be attributed not only to the energetic interaction between both components, but also to the fact that, in real solutions, the entropy of mixing may not be equal to that in an ideal system. If molecules of a component can be arranged among molecules of the other component in a greater number of ways than among those of the same kind, the entropy of a solution will be higher than the ideal entropy of mixing. Of course,

this will cause negative deviations from Raoult's law. Such a phenomenon is especially important when solutions of polymers are concerned; in their solutions, the molecules of a solute are anisodiametric and flexible, and this increases the entropy of mixing. Conversely, if the molecules of a component are arranged among those of the other in less ways than among those of the same kind, the entropy of mixing will be less than that of an ideal system. This is observed when a solute prevents the molecules of a solvent to move freely in a solution.

Raoult's law, which connects the pressure of solvent vapour above a solution and the concentration of a solute, can be used for determining the molecular weight of a solute. At first, the ratio of vapour pressures p_1/p_1^0, equal to N_1, can be found empirically, and then the molecular weight of a solute can be calculated from the equation

$$N_1 = \frac{n_1}{n_1 + n_2} = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \qquad (14.20)$$

where n_1 and n_2 = number of moles of a solvent and of a solute, respectively, in an ideal solution;

m_1 and m_2 = mass of a solvent and that of a solute, respectively;

M_1 and M_2 = molecular weights of a solvent and of a solute, respectively.

Since the value of p_1/p_1^0 is not equal to that of N_1 for polymer solutions, such a method of determining the molecular weight is unsuitable for them. But if we suppose that solutions of macromolecular substances behave as ideal solutions and if we determine p_1/p_1^0, we can calculate the *apparent*, or equivalent, molecular weight of a polymer, i.e., a quantity which is equivalent to the molecular weight of a substance that would produce an ideal solution in a given solvent.

The apparent molecular weight is the molecular weight of a chain segment which is a kinetic unit in a solution. The segment of sufficiently long molecules should not depend on the molecular weight, and the values of the apparent molecular weight are always less than those of the true molecular weight. But the more dilute are the solutions taken for determination, the closer are the values of the apparent molecular weight to those of the true one. At the limit, when the dilution of a solution is infinite, the apparent molecular weight can become equal to the true one because the kinetic unit in such a solution is the entire macromolecule. This can be used to find the true molecular weight.

However, the length of a macromolecular segment in a solution is determined not only by chain flexibility, but also by the association of macromolecules or their parts. Association depends on both the nature of a solvent and that of macromolecules, i.e., on

their content of polar or ionogenic groups by which a bond can be formed. Thus, the apparent molecular weight is a nominal quantity.

Since the molar fraction of polymers in a solution is usually very small because of their high molecular weight, a relative drop in the pressure of solvent vapour even above concentrated solutions of macromolecular compounds is very small and its experimental determination is extremely difficult. Therefore, to estimate the molecular weight, the molar fraction of a solute is found by osmotic pressure which also depends on the concentration of a solution, rather than the pressure of solvent vapour above a solution.

Osmotic pressure. The osmotic pressure π of sufficiently diluted solutions of low-molecular-weight substances obeys van't Hoff's law

$$\pi = (c/M)\, RT \qquad (14.21)$$

where c = weight concentration;
M = mass of one mole;
R = universal gas constant;
T = absolute temperature.

Van't Hoff's equation appears to be similar to the equation of state of an ideal gas. But this similarity is purely formal. Osmotic pressure has nothing in common with gas pressure, and therefore it cannot be regarded as the result of the mechanical collisions of molecules against a vessel wall. Osmotic pressure is engendered when a solvent passes into a solution through a membrane until its flow is compensated by a solvent counterflow from an osmotic cell which originates when the liquid level in an osmometric capillary rises. Osmotic pressure is measured by pressure from the solution, i.e. hydrostatic pressure, when a system is in equilibrium.

Van't Hoff's law as such cannot be applied to polymer solutions. Experiments have shown that the osmotic pressure of polymer solutions is considerably higher than required by the law. This occurs because a macromolecule owing to its flexibility behaves in a solution like several shorter molecules, i.e., it is no longer the macromolecule, but its segment, that acts as a kinetic element. Of course, all other conditions being equal, the more flexible is a molecule, the higher is osmotic pressure and the more does it deviate from the value calculated by van't Hoff's equation. Moreover, as concentration increases, the osmotic pressure of polymer solutions grows not linearly, whereas, according to van't Hoff's law, this pressure increases in direct proportion to concentration.

Fig. 14.8 schematically illustrates changes, with a growth of concentration, in the osmotic pressure of solutions of a low-molecular-weight substance (sugar), a weak electrolyte, and a macromolecular compound. The osmotic pressure of a sugar solution grows in direct

proportion to concentration. In the case of a weak electrolyte, when the osmotic pressure of a solution is caused by the number of not only molecules, but also ions, this pressure grows more slowly than concentration (see the convexity of the curve towards the ordinate). This occurs because the degree of ionization decreases as concentration increases. Lastly, the osmotic pressure of a macromolecular

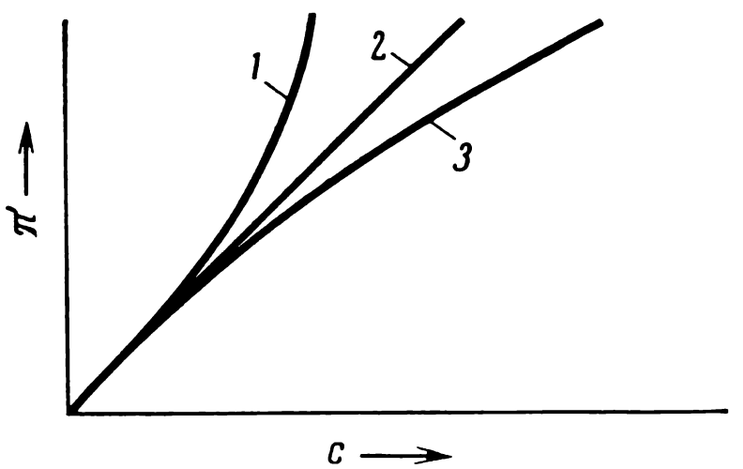

Fig. 14.8. Dependence of osmotic pressure on the concentration c of a solution: *1*—macromolecular substance; *2*—low-molecular-weight substance (sugar); *3*—weak electrolyte

solution grows more rapidly than concentration. According to Haller, this is because the number of segments, into which a flexible molecule can be arbitrarily divided, increases as concentration grows. W. Haller's concepts were the basis for proposing the following equation to describe the dependence of osmotic pressure on polymer concentration:

$$\pi = cRT/M + bc^2 \qquad (14.22)$$

where b = second virial coefficient; in the given case it is a constant characterizing the deviation from van't Hoff's equation, which depends on the nature of a solvent and of a solute, but which does not depend on the molecular weight of a solute.

When the values of c are low, the quantity of the second term of the right-hand member of the equation approximates zero and the expression assumes the form of van't Hoff's equation. Eq. (14.22) can be rewritten as

$$\pi/c = RT/M + bc \qquad (14.23)$$

In this form, the equation represents an equation of a straight line by which the molecular weight of a polymer can be easily found graphically. To this end, osmotic pressure is determined at various concentrations, a graph is plotted in the π/c, c coordinates, and the straight line is extrapolated to intersect the ordinate. The segment cut off by the straight line on the ordinate is equal to RT/M while b

is determined as the tangent of an angle formed by the straight line and the abscissa.

Fig. 14.9 illustrates the dependence of π/c on c for a solution of cellulose nitrate in cyclohexanone and a solution of hemoglobin in water; these polymers having almost the same molecular weight (70,000) are taken in order to facilitate comparison. For cellulose nitrate whose molecules are linear, the value of π/c grows as c increases, and this is caused by a growth in the number of segments with concentration; for hemoglobin whose molecules are spherical, the value of π/c does not depend on concentration.

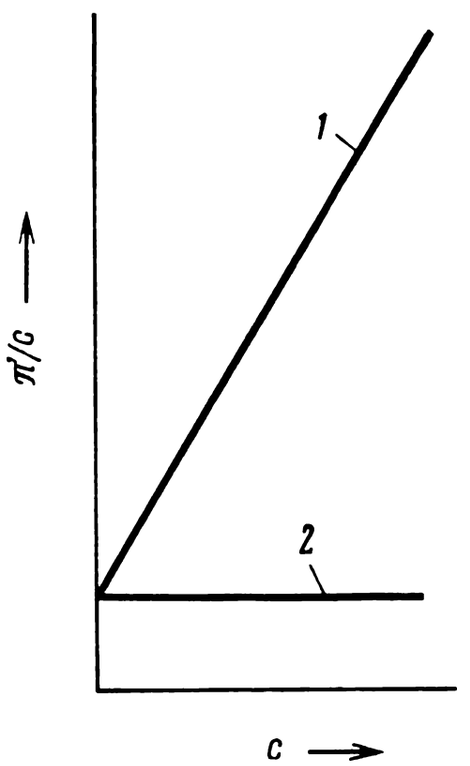

Fig. 14.9. Dependence of π/c on the concentration c of a solution:
1—cellulose nitrate in cyclohexanone; *2*—hemoglobin in water

The determination of the molecular weight by the osmotic pressure of diluted solutions is most commonly used now. Since polymer solutions can be rather easily purified, the mean molecular weights found by this method are far more reliable than the numerical weights determined by the same method for colloidal systems. There may be inaccuracies in the determination of the molecular weight by the osmotic method mainly because molecules tend to associate. Therefore, in order to avoid errors, it is expedient to determine the molecular weight of a polymer by finding the osmotic pressure of its solutions in several solvents.

As we have already seen, the molecular weight determined osmometrically is averaged out by the number of particles; this is the number-average molecular weight M_n because osmotic pressure is proportional to the number of solute molecules.

The way of preparing a solution can considerably affect osmotic pressure in sufficiently concentrated polymer solutions. Preliminary heating and stirring increase osmotic pressure whereas cooling or the long aging of a solution decreases it. These phenomena are due to the formation of associates or even three-dimensional networks of macromolecules in sufficiently concentrated polymer solutions and their destruction when a solution is stirred or heated.

Diffusion and sedimentation. Solutions of macromolecular substances are similar to typical colloidal systems by their low diffu-

sivity owing to the large dimensions of macromolecules. Nevertheless, the determination of diffusivity is widely used for establishing the molecular weight of polymers, such as proteins.

The molecular weight of polymers having spherical molecules is determined by the diffusion method in the same way as the numerical weight of colloidal systems is found by that method. At first, diffusivity is determined experimentally; then, the molecular radius is calculated by Einstein's equation and, when the molecular radius and the density of a solute are known, the mass of one mole of the solute is found.

It is far more difficult to determine the molecular weight of thread-like flexible molecules by the diffusion method because such molecules diffuse differently from spherical particles, to which Einstein's equation in its ordinary form is only applicable. Therefore, the dissymmetry coefficient must be taken into account in calculations.

The most commonly used method of determining the diffusivity of macromolecular substances is Lamm's method whereby a scale is photographed through a column of a liquid in which diffusion is occurring. Owing to the difference in refractive indices engendered by the concentration gradient in a liquid, the spacings between scale divisions on the photograph will be different from those on a photograph taken through a pure solvent. The distribution of the concentration gradient along the liquid column at different durations of diffusion can be determined by measuring the discrepancies in spacings after definite lengths of time, and then diffusivity can be calculated.

Although the solutions of macromolecular compounds have low diffusivity, they as a rule possess high sedimentation stability due largely to the low density of a solute. Therefore, the molecular weight of polymers can be determined by the sedimentation method only with the aid of a powerful ultracentrifuge.

Two methods are used for determining the molecular weight of polymers, just as for determining the numerical weight of colloidal systems: by the sedimentation rate and by sedimentation equilibrium. The advantage of the second method is that the results do not depend on the particle shape, and its disadvantage is that the establishment of sedimentation equilibrium takes a long time.

It becomes very difficult to interpret the results obtained by these methods when a solution has loose coils of flexible molecular chains instead of compact particles. If molecules are compact, their interaction is not great, its effect becomes noticeable only at high concentrations, and the results can be easily extrapolated down to zero concentration. When loose molecular coils are being investigated, difficulties arise owing to the interaction between macromolecules and the hydrodynamics of their sedimentation. In this case, the

sedimentation rate changes so rapidly with a growth in concentration that extrapolation can cause great errors.

Optical properties. Polymer chain molecules cannot be detected in solutions by ultramicroscopic observations because polymer solutions are homogeneous and linear macromolecules approximate colloidal particles only in length whereas in two other dimensions they correspond to ordinary molecules. Moreover, linear macromolecules cannot be detected under the ultramicroscope owing to their solvation (if it occurs) and to the fact that the refractive index of polymers is as a rule similar to that of a medium.

Solutions of macromolecular substances are capable of scattering light although less than typical colloidal systems. Debye proposed an optical method for determining the molecular weight of polymers by measuring the turbidity of their diluted solutions, i.e., by finding the coefficient of light extinction caused by light scattering when a beam passes through a solution layer of a definite thickness.

Concentrated polymer solutions scatter light owing to their heterogeneity caused by continuous small deviations of concentration which in turn cause fluctuations of the refractive index from its mean value.

According to Einstein,

$$\tau = \frac{32\pi^3}{3} \cdot \frac{n_0^2}{N_A \lambda^4} \cdot \frac{(\partial n/\partial c)^2 c}{\partial [\pi/(RT)]/\partial c} = \frac{Hc}{\partial [\pi/(RT)]/\partial c} \qquad (14.24)$$

where τ = turbidity of a solution;

n_0 and n = refractive indices of a solvent and of a solution, respectively;

$\partial n/\partial c$ = concentration gradient of the refractive index of a solution (a constant which can be replaced by $(n - n_0)/c$ because the difference $(n - n_0)$ is proportional to c within the region of concentrations used in determination);

λ = wavelength of incident light;

$\partial [\pi/(RT)]/\partial c$ = concentration gradient of osmotic pressure;

H = constant for a given system, being equal to $32\pi^3 n_0^2 (\partial n/\partial c)^2 (3N_A\lambda^4)$;

N_A = Avogadro number.

The inverse dependence of τ on the concentration gradient of osmotic pressure corresponds to Einstein's principle that density fluctuations in a solution are the greater, the less is osmotic pressure.

Eq. (14.24) can be rewritten as

$$\frac{Hc}{\tau} = \frac{\partial [\pi/(RT)]}{\partial c} \qquad (14.25)$$

The osmotic pressure of polymer solutions having linear molecules can be expressed by Eq. (14.22)

$$\pi = cRT/M + bc^2$$

where constant b takes account of the deviation from an ideal solution.

Substituting Eq. (14.22) in Eq. (14.25), we obtain

$$H\frac{c}{\tau} = \frac{\partial[\pi/(RT)]}{\partial c} = \frac{\partial[RTc/(MRT) + bc^2/(RT)]}{\partial c} =$$

$$= \frac{\partial c/M + b\,\partial c^2/(RT)}{\partial c} = \frac{1}{M} + 2Bc \qquad (14.26)$$

where $B = b/(RT)$.

The factor B characterizes the interaction between solute molecules. At $B = 0$, Eq. (14.26) becomes

$$Hc/\tau = 1/M$$

It follows from Eq. (14.26) that the quantity Hc/τ depends linearly on c. Such a dependence is represented in Fig. 14.10. Apparently, the segment cut off by a straight line on the ordinate is numerically equal to the quantity $1/M$.

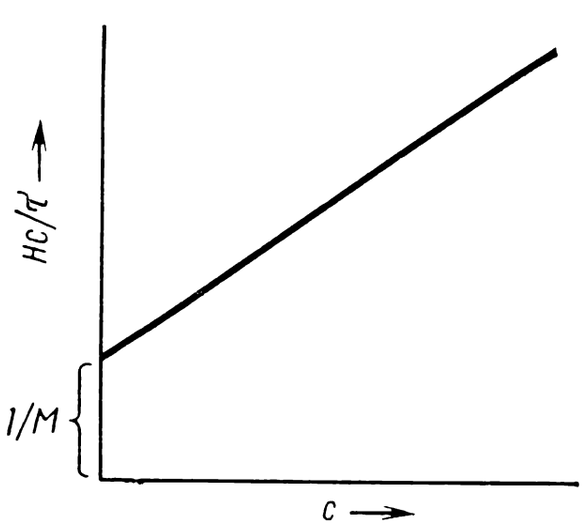

Fig. 14.10. Dependence of Hc/τ on the concentration c of polymer solutions

To determine the molecular weight by the method described above, work is done with solutions containing about 0.1 per cent of a polymer. Of course, in order to obtain correct results, test solutions must be completely free from foreign particles which are capable of scattering light. Work is done in the order given below.

1. n_0 and n are measured for some concentration of a solution. Since the difference $(n - n_0)$ in Eq. (14.24) is squared, it must be measured with very high precision.

2. τ is measured with a photometer or a nephelometer for several values of c.

3. A graph is plotted in the coordinates Hc/τ, c, the value of Hc/τ equal to $1/M$ is found at $c \to 0$, and M is calculated. The value found for polydispersed polymers is the weight-average value of the molecular weight M_G.

The optical method of determining the molecular weight can be used only when particles are smaller than 0.1 of the wavelength of scattered light. This condition is usually met only for solutions of polymers in which macromolecules are coiled.

The method described above makes it possible to determine also the interaction between a polymer and a solvent that is characterized by the deviation of a system from the behaviour of an ideal solution.

Apart from scattering light, polymer solutions can selectively absorb it. The ultraviolet and infrared absorption spectra can be used to determine the structure of a polymer: the presence of definite atomic groups in its molecules, conjugated double bonds, and so forth. However, since these methods are used for studying the solutions of not only polymers, but organic substances in general, we will not deal with them here.

Viscosity. The viscosity of solutions containing macromolecules is usually higher than that of solutions of low-molecular-weight compounds and that of colloidal solutions of the same concentrations. For example, unusually high viscosity of rubber solutions is observed already at concentrations about 0.05 per cent. Only very dilute solutions of macromolecular compounds can be assumed to obey Newton's and Poiseuille's laws. The viscosity of polymer solutions does not obey Einstein's law as well and grows with concentration. This dependence is represented graphically by a curve convex towards the concentration axis.

For a long time, the high viscosity of polymer solutions was attributed to great solvation of macromolecules. But when macromolecular solvation was found to be inconsiderable, it was believed that the viscosity of polymer solutions deviates from the laws obeyed by solutions of low-molecular-weight substances owing to the specific hydrodynamics of systems containing stretched-out flexible macromolecules and to the presence of associates and readily disintegrating structures in them.

Let us at first consider greatly diluted solutions of polymers in which macromolecules do not interact with one another. Staudinger believed that macromolecules behave in a solution as rigid rods; he proposed the following dependence of specific viscosity η_{sp} on the concentration of polymer solutions:

$$\eta_{sp} = K_M M c \qquad (14.27)$$

where K_M = constant for every polymer homologous series;
M = molecular weight of a dissolved polymer;
c = concentration of a solution expressed in "primary moles" per litre ("primary mole" is the number of grams equal to the molecular weight of a monomer from which a polymer molecule is obtained; for example, the "primary" molar solution of polybutadiene must contain 54 g of a polymer per litre).

Eq. (14.27) represented as

$$M = \eta_{sp}/(K_M c) \tag{14.28}$$

can be used to calculate the molecular weight of a polymer if the specific viscosity of its solution is determined, and its concentration c and constant K_M are known.

To find the value of constant K_M for determining the molecular weight Staudinger measured the molecular weights of the lower members of a given polymer homologous series cryoscopically, and found the specific viscosity of their solutions. Substituting these quantities in the equation

$$K_M = \eta_{sp}/(Mc) \tag{14.29}$$

he calculated the value of K_M of a given polymer homologous series.

Eq. (14.27) can be represented as:

$$\eta_{sp}/c = K_M M \tag{14.30}$$

In such a form, the equation indicates the linear relationship between the quantity η_{sp}/c, known as *reduced* (to a unit of concentration) *viscosity*, and the molecular weight of a polymer. Eq. (14.30) also shows that reduced viscosity for the same polymer (at constant molecular weight) does not depend on concentration, as is represented in Fig. 14.11 (curve *1*).

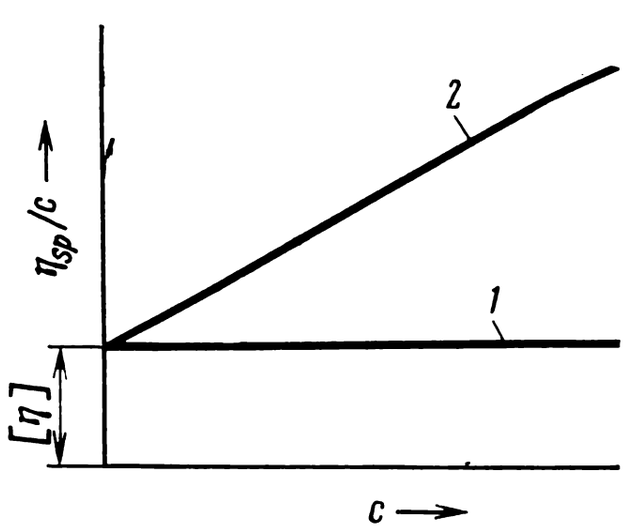

Fig. 14.11. Dependence of reduced viscosity on the concentration c of a solution:
1—solution obeying Eq. (14.30); *2*—polymer solution

The first investigations carried out by Staudinger seemed to confirm his equation. But further work has shown that the reduced viscosity of solutions of the same polymer usually grows with concentration, and this growth, in the range of small concentrations, occurs along a straight line, as is shown in Fig. 14.11 (curve *2*). The segment cut off by the straight line on the ordinate corresponds to *intrinsic viscosity* $[\eta]$ which expresses the hydrodynamic resistance to the flow of molecules of a given polymer. Intrinsic viscosity is reduced viscosity when a solution is diluted to an infinitely great extent.

Apparently,

$$[\eta] = \lim_{c \to 0} (\eta_{sp}/c) \tag{14.31}$$

and the straight-line equation in this case can be represented as

$$\eta_{sp}/c = [\eta] + ac \tag{14.32}$$

where a is the tangent of an angle formed by a straight line with the concentration axis.

The dependence of the value of η_{sp}/c on concentration should be attributed to macromolecular interaction.

The constant K_M in Staudinger's equation was found to depend in many cases on the molecular weight of a polymer, as a rule, decreasing as it increases. According to Staudinger, K_M is affected by macromolecular branching which usually grows with the degree of polymerization. But it has been ascertained that the value of K_M decreases as the molecular weight increases also for strictly linear molecules.

M. Huggins has shown that a change in K_M with an increase in the molecular weight is due not to greater macromolecular branching, but to the fact that longer molecules can bend more and thus offer less resistance to liquid flow.

The molecular weight is determined now by the following equation which takes account of both macromolecular interaction even in diluted solutions, and a change in constant K_M as molecular length changes

$$[\eta] = kM^a \tag{14.33}$$

where k = coefficient which is constant for the solutions of compounds of a polymer homologous series in a given solvent;
a = quantity which characterizes the shape of macromolecules in a solution and depends on chain flexibility.

If $a = 1$, the equation becomes similar to Staudinger's equation. But if $a = 0$, Eq. (14.33) becomes Einstein's equation, derived from the assumption that particles are spherical, according to which solution viscosity does not depend on particle dimensions.

The shape of macromolecules in a solution was found to be considerably affected by the nature of a solvent. Polymer molecules may be more stretched out in one solvent whereas in another they may be more coiled. As a rule, the better does a polymer dissolve in a given liquid and the more is it solvated, the less do molecular chain parts interact with one another, the more stretched out are macromolecules, and the higher is solution viscosity. In a bad solvent, macromolecules are poorly solvated and therefore form more compact coils. That is why solution viscosity decreases considerably when a non-solvent is added to a polymer solution.

Thus, the hydrodynamic resistance of macromolecules to liquid flow and, consequently, intrinsic viscosity will change for the same polymer dissolved in various solvents. It has been found that the

dependence of η_{sp}/c on concentration is affected by the nature of a solvent, i.e., the slope of the straight lines η_{sp}/c, c changes. It is assumed from certain considerations that the coefficient which determines the slope of a straight line is proportional to the square of $[\eta]$. Eq. (14.32) can then be written as

$$\eta_{sp}/c = [\eta] + k[\eta]^2 c \qquad (14.34)$$

M. Huggins believes that coefficient k in this equation can characterize the intensity of interaction between molecules of a polymer and a solvent.

To calculate the molecular weight by Eq. (14.33), the quantities k and a must be known. They are calculated by the experimentally found values of solution viscosity and by the molecular weight of a member of a given polymer homologous series that has been determined by a more precise method. Table 14.4 gives the values of k and a for some polymers. For molecular weights which are lower than those indicated in the last column of the Table, the values of a for all polymers gradually approximate unity in conformity with Staudinger's original equation.

Table 14.4. **Values of k and a for the Viscometric Determination of Molecular Weights of Some Polymers by Eq. (14.33)**

Polymer	Solvent	Temperature, °C	$k \cdot 10^4$	a	Molecular weight region, $M \cdot 10^{-5}$
Cellulose	Cuprammonium solution	25	0.85	0.81	—
Polyisobutylene	Diisobutylene	20	3.6	0.64	0.05-13.0
Natural rubber	Toluene	20	5.02	0.67	0.4-15.0
Polystyrene	Toluene	30	3.7	0.62	2.0-18.0
Polymethyl methacrylate	Chloroform	20	0.49	0.82	0.56-9.8
Polyvinyl acetate	Acetone	50	2.8	0.67	0.77-8.5

Let us now consider the viscosity of solutions of average concentration which do not obey Newton's and Poiseuille's laws. The viscosity coefficient for these solutions is not constant, but depends on the gradient of the rate or pressure if a determination is being made with a capillary viscometer. In this case, like for cross-linked colloidal systems, solution viscosity decreases, gradually approaching a certain limit, as the rate gradient increases.

Viscosity depends on the rate gradient for polymer solutions of average concentration because of two reasons.

First of all, as a solution flows, long coiled molecular chains straighten out and orient towards flow, and this reduces the hydrodynamic resistance to flow. This is similar to the dependence of the viscosity coefficient on the rate gradient for colloidal systems containing rigid elongated particles. Of course, macromolecules orient themselves also in the flow of diluted polymer solutions. However, in this case, deviations from Poiseuille's law are considerably less owing to the low concentration of a dispersed phase in a solution. At a very high rate of flow, molecular chains can stretch out so greatly that macromolecules rupture. This probably explains why polymers are somewhat depolymerized in solutions as they flow at a very high rate through thin capillaries.

Secondly, in sufficiently concentrated solutions, macromolecules can interact with one another and form associates or even pieces of a three-dimensional network that greatly hinder flow. As flow accelerates, these structures gradually disintegrate, and this also must reduce the resistance of molecules to flow and, consequently, solution viscosity. Such an explanation is quite similar to that offered for such a phenomenon involving cross-linked colloidal systems.

Trapeznikov used new methods of measurement and devices to study the rheological properties of concentrated solutions of polymers mainly in non-polar solvents. He determined shearing stress as well as recoverable strain, not only in stationary flow, but also at the pre-stationary stage of strain. These investigations have shown that many systems possess properties characteristic of both typical plastic systems and liquids which do not obey Newton's law and whose viscosity in flow is determined by molecular orientation. To explain these properties, it is necessary to reject the ordinary concept that flow is impossible below the yield point. If irreversible relaxation is in principle possible at any low shearing stresses, flow is also possible at the same low stresses. The duration of measurement and the sensitivity of recorders should only be increased. In this connection, a new concept of the yield point was proposed to indicate not the appearance of flow, but a change in the flow rate caused by structural changes in a system.

As temperature rises, the intensity of the motion of segments increases, and this hinders the formation of structures; as a result, there is less deviation from Newton's and Poiseuille's laws at elevated temperature. In addition, the true coefficient of internal friction decreases as temperature rises, and this also causes a diminution in solution viscosity. However, an elevation of temperature does not always cause a diminution in the viscosity of a polymer solution. Such a diminution is characteristic of solutions containing greatly branched macromolecules whose segmentary motion is expressed poorly. The viscosity of solutions containing long un-

branched molecular chains can even increase with temperature, owing to the greater intensity of segmentary motion which hinders the orientation of macromolecules in flow.

Besides the dependence of the viscosity coefficient on the rate gradient, other anomalies are observed for solutions of average concentration, such as an increase in viscosity when a solution is allowed to stand, a decrease in viscosity when it is heated and subsequently cooled, when it is stirred, and so forth. All these anomalies are the result of the non-equilibrium state of a solution, and occur because a system tends to become cross-linked.

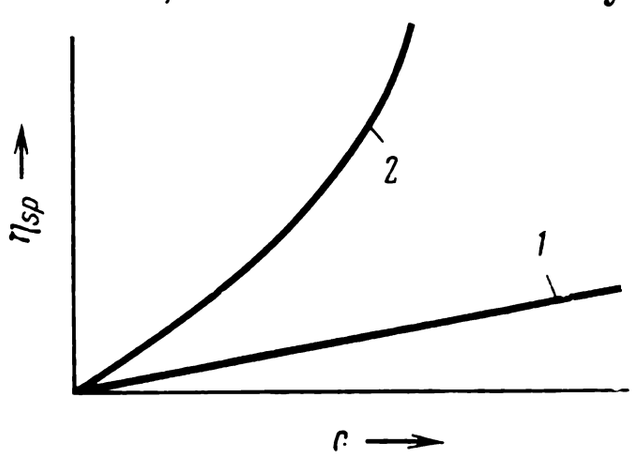

Fig. 14.12. Dependence of specific viscosity on the concentration c of an aqueous solution:
1—sugar; *2*—sodium caseinate

The viscosity of polymer solutions often changes with an increase in their concentration. Fig. 14.12 schematically illustrates the dependence of η_{sp} on c for aqueous solutions of sugar and sodium caseinate. As we may see, this dependence for the sugar solution is expressed by a straight line. The polymer solution of sodium caseinate behaves quite differently. As concentration increases, its viscosity grows very sharply following the curve which is convex towards the abscissa. A purely qualitative explanation of such an anomaly is that the effective volume, i.e., the volume of a system minus the volume of macromolecules, rather than the total volume of a system, must enter Einstein's equation (like van der Waals' equation). Since macromolecules in the solution are coiled and contain a large amount of a solvent, the volume of the solvent, being strongly bound to the polymer, should also be related to the volume of a dispersed phase (for more details, see Chap. 10).

Viscosity may sharply increase with concentration also as a result of the formation of structures in a system. Here, a solution possesses structural viscosity whereas, in the first explanation of the concentration anomaly, an allowance does not have to be made for macromolecular interaction.

Viscosity, like the osmotic pressure of sufficiently concentrated solutions of macromolecular substances, can be affected by the technique of preparing a solution. Such an effect is likewise attributed to the slow establishment of equilibrium in a system.

The viscosity of solutions of macromolecular substances can be affected when small amounts of some substances are introduced into a solution. For example, as ethanol or water are added in a growing amount to solutions of cellulose ethers, their viscosity

at first decreases, and then increases. Viscosity of these solutions increases when the salts of aluminium, iron, lead, calcium, magnesium and zinc are added to them, and it decreases when some soaps are introduced.

The viscosity of solutions of macromolecular substances increases when some substances are added to them because macromolecules interact to a greater extent as active sites on molecular chains become free under the action of impurities, or because chemical bonds are formed between molecules of a polymer and impurities (such as metal oxides and aldehydes). A decrease in viscosity can be attributed either to the destruction of macromolecules under the action of impurities (ammonia, aldehydes, acids, etc.) or to a diminution in the interaction between chains as chemical bonds are formed between impurities and active macromolecular groups.

Solutions of macromolecular substances do not obey Walden's rule which claims that the equivalent electric conductivity λ of ordinary viscous solutions containing low-molecular-weight electrolytes is inversely proportional to viscosity, i.e.,

$$\lambda = k\,(1/\eta) \tag{14.35}$$

or

$$\lambda\eta = \text{const} \tag{14.36}$$

In polymer solutions whose viscosity is determined by the presence of long coiled chain molecules, the ions of low-molecular-weight electrolytes are capable of moving quite freely in an aqueous medium between the macromolecules. As a result, the electric conductivity of viscous polymer solutions containing low-molecular-weight eletrolytes is almost equal to the conductivity of the solutions of these electrolytes. It is therefore clear why the electric conductivity of solutions of macromolecular substances does not depend on their viscosity, even when a polymer solution becomes a gel.

Aggregative stability. Solutions of macromolecular substances, like true solutions, are aggregatively stable if they are in a state of thermodynamic equilibrium. Kruyt and Bundenberg de Jong ascribed the aggregative stability of lyophilic colloidal systems such as solutions of gelatin, agar, and other polymers to the electric charge of particles, their solvation, or the simultaneous action of both factors, but their theories are now only of historic interest.

Polymers separate from a solution when large amounts of electrolytes are introduced into it. But this phenomenon should not be identified with the coagulation of typical colloidal systems. Sols coagulate when rather small amounts of an electrolyte are introduced, and it is an irreversible process. A polymer separates from a solution when relatively large amounts of an electrolyte are added; the process does not obey the Schulze-Hardy rule and is usually

reversible: a macromolecular substance can dissolve again when an electrolyte is removed from a precipitate by either washing or dialysis.

The mechanisms of the two phenomena are also different. Sols coagulate usually due to the compression of the electric double layer, and to either the diminution or complete disappearance of the electric charge on the particle surface; here, the charge is the main factor of stability. A polymer separates from a solution when an electrolyte is added because it becomes less soluble in a concentrated electrolytic solution. This process can be called "salting out" by analogy with similar phenomena in solutions of low-molecular-weight substances. Debye believes that, in the salting-out process, molecules of a solute are displaced from the electric field of ions which are bound to polar solvent molecules. Thus, the salting-out process does not differ in principle from the separation of a polymer from a solution when a non-solvent is added to the latter. As a rule, the salting-out effect of ions changes in the order in which they are in a lyotropic series. Thus, cations can be arranged in the following series as their salting-out effect diminishes:

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

A similar series of anions has the following form:

$$SO_4^{2-} > Cl^- > NO_3^- > Br^- > I^- > NCS^-$$

The relationship between the salting-out effect and the place of an ion in a lyotropic series is quite clear: the more is an ion capable of binding a solvent, the more will it reduce the ability of a medium to dissolve a macromolecular substance.

The salting-out process is used in fractionating macromolecular substances because the ability of these compounds to separate from a solution depends on their chemical nature and increases with the molecular weight. Fractionation by salting-out is often employed to isolate proteins. In this case, the salting-out process is combined with the introduction of a non-solvent, e.g., ethanol, into a system and the cooling of a solution. It is expedient to salt out proteins at a pH value which is close to the isoelectric point because the charge and hydration of protein molecules grow and their solubility increases when the pH value is either higher or lower than the isoelectric point.

Coacervation is sometimes observed in solutions of macromolecular compounds when temperature or pH changes or low-molecular-weight substances are introduced. This phenomenon is characteristic only of solutions that are not in thermodynamic equilibrium; it consists in the separation of a system into two phases: one is a solution of a polymer in a solvent, and the other, a solution of a solvent in a polymer. A solution richer in a macromolecular substance separa-

tes as minute droplets. If the solvent is a polar liquid, such as water, these droplets can get charged under definite conditions, this being proven by their ability to undergo electrophoresis. The electric charge of the droplets imparts stability to these systems which are in general thermodynamically out of equilibrium. Such systems, known as coacervates, are similar to typical emulsions and are supposed to be involved in the living organisms.

If minute droplets of coacervates do not possess sufficient aggregative stability and at the same time are incapable of coalescing, they combine with one another, forming flocculi which either float up or settle to the bottom of a vessel as a loose precipitate. Such flocculation occurs when a phase having a large content of a macromolecular component is sufficiently viscous. If the viscosity of a phase is low, individual minute droplets coalesce to form larger drops. When a system in which coacervation occurred stands for a long time, two homogeneous liquid layers consisting of phases with a different polymer content are formed. Permanent three-dimensional networks can originate in sufficiently concentrated polymer solutions owing to the cohesion of macromolecules, and then the solution becomes a gel.

Let us now deal briefly with the aging of polymer solutions. It is usually believed that aging is exhibited most clearly in the spontaneous change in the viscosity of equilibrium solutions. Formerly, when solutions of macromolecular substances were regarded as colloidal systems, the changes in viscosity were attributed to the slowly occurring phenomena of peptization or, conversely, aggregation. Such an explanation is unsatisfactory today, when not too concentrated solutions of macromolecular substances are known to be homogeneous.

The change in the viscosity of polymer solutions when they are allowed to stand should be attributed to the action of oxygen or other impurities, present in a system, on molecular chains. Oxygen may either destroy macromolecules or bind their individual threads into large formations. In the first case, viscosity decreases, and in the second, increases. Some other impurities can act similarly on the viscosity of polymer solutions. Thus, solutions of macromolecular compounds, unlike typical colloidal systems, are not subjected to the process of aging proper; some of their properties change on long standing due to the slow action of extraneous substances present in these solutions.

8. POLYELECTROLYTES

In the preceding sections, we considered the properties of solutions of polymers whose macromolecules do not contain ionogenic groups, such as natural and synthetic rubbers, polyisobutylene,

cellulose nitrate, cellulose acetate. However, molecules of several polymers contain ionogenic groups and are capable of dissociating into ions in solutions. Such macromolecular electrolytes, or *polyelectrolytes*, can be divided into three categories according to the nature of the ionogenic groups which they contain.

1. Polyelectrolytes containing an acid group, such as $-COO^-$ or $-OSO_3^-$. The $-COO^-$ group is contained in gum arabic, alginates, and soluble starch whereas the $-OSO_3^-$ group is found in agar.

2. Polyelectrolytes containing a basic group, such as $-NH_3^+$. Such substances are not found in nature, but they can be synthesized.

3. Polyelectrolytes containing both an acid and a basic group (polyampholytes). They include proteins having the $-COO^-$ and $-NH_3^+$ groups. Polyampholytes, such as copolymers of acrylic acid and vinyl pyridine, and of glutamic acid and lysine, have been synthesized.

Properties of solutions of polyelectrolytes. Polyelectrolytes, except proteins, are characterized by a very compact arrangement of ionogenic groups: one chain unit usually has one ionogenic group. For proteins, 6-8 residues of amino acids have a carboxylic group or an amino group. As a result, molecules of polyelectrolytes can undergo considerably great electrostatic interactions in solutions, and this highly deforms the chains of flexible molecules. Such deformation depends on the extent of group ionization which is caused by the presence of low-molecular-weight electrolytes in a system and by the pH of a solution. E. Katchalski has shown that the chains of polyacrylic acid can spontaneously stretch and contract by several times their length as the pH of a solution changes.

All the macromolecular electrolytes dissolve in polar solvents because macromolecules having ionogenic groups interact with polar liquids more strongly than with non-polar ones. Polymers were once called lyophilic colloids owing to the considerably great interaction between macromolecular electrolytes (proteins) and the medium (water).

Let us consider the most important representatives of polyelectrolytes, i.e., proteins, because their behaviour in solutions is most complicated. As for other macromolecular electrolytes containing either only acid or only basic groups, they do not have merely the properties inherent in the absent ionogenic group.

Molecules of proteins, made out of amino acids, contain the basic group $HONH_3-$ and the acid group $-COOH$ in an aqueous medium, and are therefore amphoteric compounds. The protein molecule can be schematically represented as $HONH_3-R-COOH$ where R is a sufficiently long hydrocarbon chain which contains the $-CONH-$ groups. However, the ionogenic groups $OHNH_3-$ and $-COOH$ not only can be arranged at the ends of a molecule, but also can

exist as short side chains distributed along the length of the main chain.

In an aqueous solution at a definite concentration of hydrogen ions that corresponds to the isoelectric point, the number of ionized basic groups is equal to that of ionized acid groups for any ampholyte (amphoteric electrolyte), and the number of both groups is minimum. A protein molecule in an isoelectric state should be regarded on the whole as neutral although it has ionized groups. It can schematically be represented in this state in the following way:

$$OH^- + NH_3^+ - R - COO^- + H^+$$

Since most proteins are more acidic than basic, their isoelectric point is below pH 7. In other words, in order to reach the isoelectric point, a protein solution should contain an amount of acid that suppresses the excess ionization of acidic groups. Since the number of interacting ionized basic and acid groups in a molecule is the same at the isoelectric point, a flexible macromolecule coils in this state. Owing to the attractive forces acting between charged groups of different signs, the density of the coil will be greater than that which corresponds to the most statistically probable shape of a macromolecule or to its maximum entropy.

In an acid medium, say in the presence of HCl, when the ionization of carboxylic groups is suppressed by an excess of hydrogen ions, the following reaction occurs:

$$OH^- + NH_3^+ - R - COOH + H^+ + Cl^- \longrightarrow Cl^- + NH_3^+ - R - COOH + H_2O$$

A protein molecule, acting here as a base, acquires a positive charge and migrates to the cathode in electrophoresis. Since electric repulsive forces act between charged groups of the same sign that are scattered along the length of a molecule, a coiled chain of a protein molecule will tend to straighten out in an acid medium. As a result, the density of a molecular coil decreases and can be even lower than that which corresponds to the most statistically probable shape of a flexible macromolecule. However, when the excess of HCl is high, the degree of ionization of the $ClNH_3-R-COOH$ compound, being a salt of a strong acid and a weak base, will decrease owing to the presence of a large amount of chloride ions, and the molecule will wind again into a compact coil.

In an alkaline medium, such as in the presence of NaOH, the ionization of the $HONH_3-$ groups is suppressed by a large amount of hydroxyl ions in a solution, and the following reaction occurs in it:

$$HONH_3 - R - COO^- + H^+ + Na^+ + OH^- \longrightarrow HONH_3 - R - COO^- + Na^+ + H_2O$$

The protein molecule acts like an acid; it acquires a negative charge and migrates in electrophoresis towards the anode. In this case, a

chain molecule tends to straighten out as a result of the interaction between the charged $-COO^-$ groups of the same sign, and the density of the molecular coil decreases. But when there is an excess of NaOH, the charge will diminish due to the presence of a large amount of Na^+ ions and to a decrease in the ionization of the $HONH_3—R—COONa$ salt, and the macromolecule will wind again into a compact coil.

The shape of macromolecules is affected not only by a change in the pH of a medium, but also by the introduction of an indifferent electrolyte into a solution. When the amount of an electrolyte in a polyelectrolytic solution is not too large, the ionization of ionogenic groups is suppressed and the macromolecule acquires the most statistically probable conformation. When the concentrations of electrolytes are high, their salting-out effect reduces the solubility of polymers and causes the formation of compact molecular coils. In this case, the action of ions of low-molecular-weight electrolytes will correspond to the order in which they are arranged in the lyotropic series.

The molecules of a macromolecular electrolyte possess all the properties of ordinary electrolytes, including the ability to suppress the ionization of other electrolytes. Therefore, an increase in the concentration of a macromolecular electrolyte in a solution will act in the same way as when an indifferent electrolyte is introduced into a system.

It follows that pH and electrolytes affect the charge and shape of molecules of macromolecular electrolytes. Apparently, these factors should also affect the properties of a solution that depend on the shape of dissolved macromolecules, such as viscosity, osmotic pressure and the volume of the gel of a swollen polymer if it does not dissolve in a given medium.

Let us see how pH affects the properties of protein solutions.

Fig. 14.13 represents the experimentally found dependence of the relative viscosity of a 0.67 per cent gelatin solution on the pH of the solution. The lowest viscosity corresponds to the isoelectric point (pH 4.8) at which a molecule is wound into the compact coil and, owing to the small volume of the coil, hinders liquid flow least of all. Solution viscosity grows both when pH decreases or increases because the coil volume becomes larger as molecules unwind. But solution viscosity diminishes again at very high and very low pH values because the molecular coil becomes more compact as the ionization of charged ionogenic groups of the same sign is suppressed.

The curve for the dependence of the volume of the gelatin gel on the pH of a liquid with which the gel is in a state of equilibrium should have a similar shape. Indeed, Loeb's experiments have shown that the extent of gelatin swelling in water, depending on pH, can be represented by a saddle-shaped curve. The curve has a minimum,

which corresponds to the isoelectric point, and two maxima on the right-hand and left-hand sides of the minimum (see Fig. 14.14).

As regards the effect of ionization of the ionogenic groups of macromolecules on the gel volume, it is expedient to deal even briefly with the investigations which have engendered the general theory of the swelling and "unswelling" of gels of macromolecular electrolytes as the extent of ionization changes.

If a load is applied to a gel of a macromolecular electrolyte, the gel is capable of performing mechanical work as its molecules are

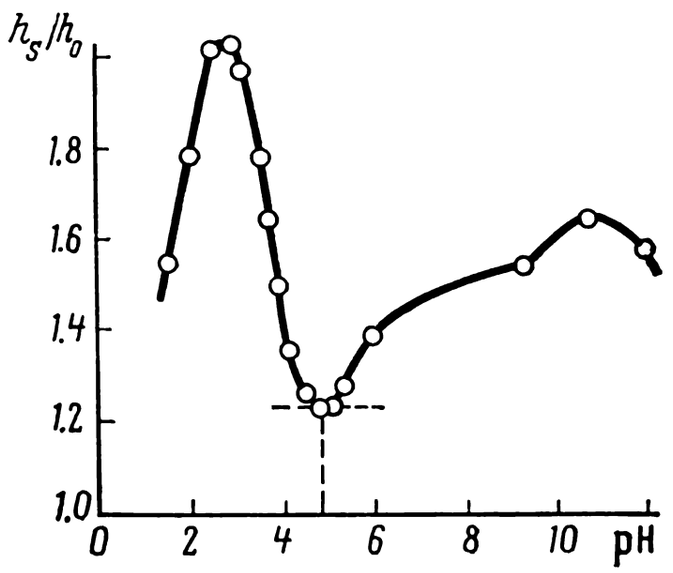

Fig. 14.13. Dependence of relative viscosity of 0.67 per cent gelatin solution on the pH of the medium

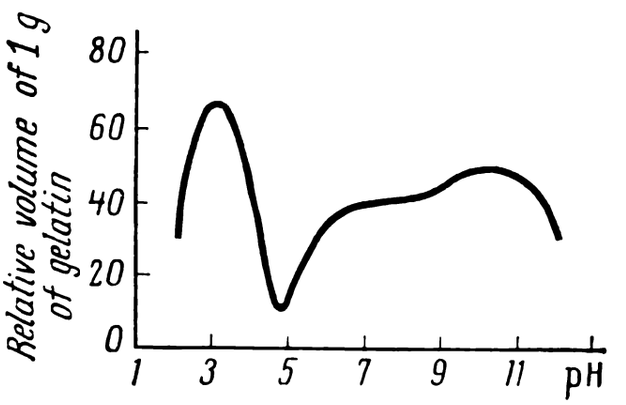

Fig. 14.14. Dependence of gelatin swelling on the pH of the medium

alternately ionized and neutralized (molarized). Thus, the gel can be a mechanical-chemical engine. The network of molecules of a macromolecular electrolyte, like a heat engine, can perform work by converting chemical energy into mechanical energy, and this may occur at constant temperature. The work of muscles of a living organism involves mechanical-chemical processes, and man is capable of doing work precisely owing to them.

Evidently, the curve which expresses the dependence of the osmotic pressure of a gelatin solution on pH should also be saddle-shaped. In an isoelectric state, a densely coiled macromolecule is rigid, and the number of segments acting as kinetic units is minimum. At pH values which are higher and lower than the isoelectric point, the gelatin macromolecule becomes more flexible as it unwinds; this causes an increase in the number of moving segments and, consequently, in osmotic pressure. When an excess of acid or alkali is added to a solution, the flexibility of the molecular chain decreases again, the number of moving segments becomes less and, consequently, the osmotic pressure of the solution drops.

Similar considerations can be used to predict how the viscosity of the solution of a macromolecular electrolyte, its osmotic pressure,

or the volume of a swelling gel will change when an indifferent electrolyte of a low molecular weight is introduced into a system.

Donnan's membrane equilibrium. The dependence of the properties of solutions of macromolecular electrolytes on pH and on the content of electrolytes of a low molecular weight can be attributed not only to a change in the shape of a macromolecule in a solution, but also to Donnan's membrane equilibrium. True, the Donnan equilibrium is a formal thermodynamic interpretation of a process, and it cannot be used to draw a conclusion on the molecular mechanism of a phenomenon. In addition, this equilibrium, like any thermodynamic interpretation of a process, is applicable only if a system is in a state of equilibrium.

Let us consider the dependence of the osmotic pressure of solutions of polyelectrolytes on pH and on the presence of electrolytes as perceived by Donnan, and then see on the basis of this conception how pH and electrolytes of a low molecular weight affect the volume of a swollen gel and the viscosity of polymer solutions.

The osmotic pressure of polymer solutions can be determined much more precisely than that of typical lyosols because solutions of macromolecular substances can be purified by long dialysis or reprecipitation without fearing coagulation. However, in practice, it is very difficult to remove all the extraneous electrolytes from the solution of a macromolecular electrolyte, and osmotic pressure has to be determined in their presence. To preclude the effect of electrolytes of a low molecular weight on the results, J. Duclaux and G. Malfitano measured the osmotic pressure of solutions of macromolecular electrolytes by putting the solution being dialyzed in an osmometer into an ultrafiltrate. However, as Donnan has shown, the results of these investigations cannot be considered to be correct.

To understand why this is so, let us suppose that in determining osmotic pressure by means of an ordinary osmometer having a semipermeable membrane, a solution of a macromolecular electrolyte is poured into an osmotic cell at the beginning of an experiment; this electrolyte completely dissociates into macromolecular ions R^{z+}, which are incapable of undergoing dialysis, and into small ions, such as Cl^-, which penetrate through the membrane. Let it be taken that the concentration of R^{z+} ions in the internal solution is c_1; the concentration of Cl^- ions in the same solution will then be zc_1. Suppose that the external liquid of an osmometer contains a low-molecular-weight electrolyte, such as sodium chloride, both ions of which (Na^+ and Cl^-) are capable of passing through the membrane. Let us denote the concentration of NaCl in the external solution by c_2. Lastly, for the sake of simplicity, let us suppose that the volumes of the internal and external solutions are equal.

Ions will then be distributed in the following way at the beginning of the experiment:

Internal liquid (*i*)	External liquid (*e*)
$[R^{z+}]_i = c_1$	$[Na^+]_e = c_2$
$[Cl^-]_i = zc_1$	$[Cl^-]_e = c_2$

It could have been supposed, like Duclax and Malfitano did, that ions of sodium chloride are distributed uniformly on both sides of the semipermeable membrane as a result of osmosis. But the experiment has shown that this is not so. Donnan had found that general equilibrium is attained in this case:

Internal liquid (*i*)	External liquid (*e*)
$]R^{z+}]_i = c_1$	$[Na^+]_e = c_2 - x$
$[Cl^-]_i = zc_1 + x$	$[Cl^-]_e = c_2 - x$
$[Na^+]_i = x$	

When equilibrium is established, ions of a low-molecular-weight electrolyte cannot penetrate through the membrane separately; otherwise, electric fields hindering diffusion would originate. The number of simultaneous collisions by Cl^- and Na^+ ions per unit area of the inner surface of the membrane depends on the product of ion concentrations, i.e., $[Na^+]_i \cdot [Cl^-]_i$. For the outer surface of the membrane, the number of simultaneous collisions of ions will be proportional to the product $[Na^+]_e \cdot [Cl^-]_e$. Apparently, equilibrium will be established in the system when the number of pairs of ions passing through the membrane from right to left per unit time will be equal to the number of pairs of ions passing from left to right. In other words, a condition of equilibrium is the equality of the products of concentrations of ions which are inside and outside the membrane and which freely pass through it:

$$[Na^+]_i \cdot [Cl^-]_i = [Na^+]_e \cdot [Cl^-]_e \qquad (14.37)$$

Substituting the values found for $[Na^+]_i$, $[Cl^-]_i$, $[Na^+]_e$ and $[Cl^-]_e$ in Eq. (14.37), we obtain

$$x\,(zc_1 + x) = (c_2 - x)^2 \qquad (14.38)$$

or

$$zc_1 x = c_2^2 - 2c_2 x \qquad (14.39)$$

whence

$$x = \frac{c_2^2}{zc_1 + 2c_2} \qquad (14.40)$$

When $c_1 \gg c_2$, i.e., when a system has a small amount of an indifferent electrolyte,

$$x = \frac{c_2^2}{zc_1} \qquad (14.41)$$

From this equation, it is easy to obtain the proportion

$$\frac{x}{c_2} = \frac{c_2}{zc_1} \tag{14.42}$$

The proportion shows that when the amount of a low-molecular-weight electrolyte is small, it will be mainly in the external liquid.

When $c_1 \ll c_2$, i.e., when a system has a large amount of an indifferent electrolyte,

$$x = \frac{c_2^2}{2c_2} = \frac{c_2}{2} \tag{14.43}$$

In other words, the electrolyte is distributed uniformly on both sides of the membrane.

The foregoing scheme relates solely to the case when a low-molecular-weight electrolyte is only in the external liquid at the beginning of the experiment. But the picture does not change considerably if this electrolyte is then present also in the osmotic cell, or if a macromolecular and a low-molecular-weight electrolytes do not have a common ion, e.g., when R^{z+} and Cl^- ions are in the internal liquid of an osmometer, and Na^+ and Br^- ions are in the external one.

Let us now determine the components of osmotic pressure in the foregoing case. If we disregard the considerations discussed above and suppose that the presence of a low-molecular-weight electrolyte has no effect because it freely passes through the membrane, the osmotic pressure could be expressed by the equation

$$\pi = RTc_1 (z + 1) \tag{14.44}$$

In fact, due to the establishment of the Donnan equilibrium, the osmotic pressure of the solution will be

$$\pi = RTc_1 + RT (zc_1 + x) + RTx - 2RT (c_2 - x) \tag{14.45}$$

where RTc_1 = osmotic pressure caused by macromolecular ions;
$RT (zc_1 + x)$ = osmotic pressure of Cl^- ions;
RTx = osmotic pressure of Na^+ ions in the cell of the osmometer;
$2RT (c_2 + x)$ = osmotic pressure of a low-molecular-weight electrolyte in the external liquid.

Substituting the value of x from Eq. (14.40) in the given equation and making some transformations, we obtain

$$\pi = \frac{RTc_1 [(z+1) zc_1 + 2c_2]}{zc_1 + 2c_2} \tag{14.46}$$

When $c_1 \gg c_2$, i.e., when the system has almost no low-molecular-weight electrolyte, Eq. (14.46) becomes

$$\pi = RTc_1 (z + 1) \qquad (14.47)$$

In other words, the osmotic pressure in this case is the pressure of a macromolecular electrolyte.

When $c_1 \ll c_2$, i.e., when a system has a large amount of a low-molecular-weight electrolyte, Eq. (14.46) becomes

$$\pi = RTc_1 \qquad (14.48)$$

This means that the osmotic pressure found here is pressure caused only by polymer ions.

As regards all the intermediate ratios between the contents of electrolytes of a high and a low molecular weights, osmotic pressure will change within the range of $RTc_1(z + 1)$ to RTc_1.

Thus, the Donnan effect must always be taken into account when investigating the osmotic pressure of solutions of macromolecular electrolytes. In order to obtain correct results, the worker either determines the concentration of electrolytes in a system and then makes the appropriate correction in the calculations, or measures osmotic pressure in the presence of an excess of a low-molecular-weight electrolyte. In the latter case, the osmotic pressure found corresponds to that of only high-molecular-weight ions.

Since osmotic equilibrium is established in the non-uniform distribution of ions on both sides of the membrane, a difference in the electric potentials between the liquids inside and outside the osmotic cell (the "membrane potential") should originate in a system. This difference can be detected by introducing, for example, the same calomel electrodes into the internal and external liquids of the osmometer. When the distribution of electrolytes in a system is known, the difference in potentials can be calculated by Nernst's equation. Loeb has shown that the values of the difference in potentials which are calculated and those which are found experimentally coincide rather well.

The theory of Donnan's membrane equilibrium makes it possible to explain the saddle-like shape of the curve which characterizes the dependence of the osmotic pressure of a protein solution on the pH of a medium. Indeed, the number of ionized ionogenic groups is minimum at the isoelectric point of an ampholyte. This is what will cause minimum pressure. When acid, such as HCl, is added, the content of anions (chloride ions) in a solution at first grows more rapidly than that of hydrogen ions which bind to the hydroxyls of hydrated amino groups of a protein to form water. This will continue until all the hydroxyl groups become bound to hydrogen ions, and the $OHNH_3$— groups are converted into the $ClNH_3$— groups. At this moment, osmotic pressure will be maximum because the $ClNH_3$— groups are ionized more strongly than the $OHNH_3$—

groups, and the system does not contain an extraneous low-molecular-weight electrolyte (HCl) which can penetrate through a membrane and reduce the osmotic pressure of the macromolecular electrolyte. When acid is added further, the number of chloride ions will grow less because the dissociation of protein molecules is suppressed in comparison with the number of chloride and hydrogen ions formed as HCl dissociates. Osmotic pressure will be caused only by polymer ions owing to an excess of a low-molecular-weight electrolyte which is distributed uniformly in the internal and external liquids of the osmometer. In addition, the dissociation of the $ClNH_3$— groups decreases because the system has an excess of chloride ions. As a result, osmotic pressure will drop when excess acid is added.

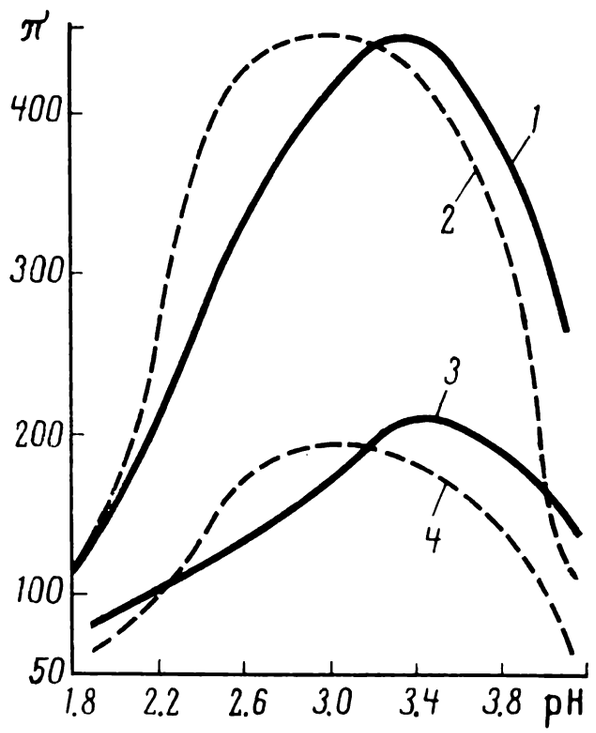

Fig. 14.15. Calculated and experimentally determined values of osmotic pressure of acidified gelatin solutions: *1*—HCl, determ.; *2*—HCl, calc.; *3*—H_2SO_4, determ.; *4*—H_2SO_4, calc.

Donnan's theory not only explains the shape of the curve which characterizes a change in osmotic pressure as pH alters. It also allows to predict that, when an acid having a divalent anion is introduced into a system, the curve should lie below the one for an acid having a monovalent anion. Fig. 14.15 shows such curves obtained by Loeb when HCl and H_2SO were added to a gelatin solution. The experimentally found curves are drawn with solid lines, and the theoretically calculated ones (according to Donnan), with dashed lines. A certain discrepancy between experimental and theoretical curves is apparently caused by a change in the degree of ionization of the $ClNH_3$— groups when acid is added.

A similar picture is observed also when pH rises: the osmotic pressure of a protein solution at first increases when alkali is added, and then, after reaching the maximum, it begins to decrease.

Donnan's theory satisfactorily explains the shape of the curves which characterize a change in osmotic pressure owing not only to the pH of a solution, but also to the introduction of neutral electrolytes. However, this case will not be considered in this textbook.

A certain dependence of the volume of a swollen protein (e.g., a gelatin gel) on the pH of a medium is also explained very simply from the standpoint of the theory of membrane equilibrium. A minimum degree of gel swelling should correspond to the isoelectric point

of the protein because osmotic pressure, being the cause of swelling, is also minimum. The curve for the dependence of volume on pH rises on both sides from this minimum and, after reaching the maximum, it drops because osmotic pressure depends on pH in the same way. In interpreting swelling from Donnan's standpoint, it makes no difference at all whether protein macromolecules are individual kinetic units or they form a three-dimensional network. In other words, it does not matter how polyvalent ions are held together in a system, whether as a result of the presence of a semipermeable membrane or whether these ions are bound to one another by strong bonds and form a three-dimensional network.

The effect of neutral electrolytes on protein swelling can be explained in a similar way. In acidic and alkaline media, all the neutral salts reduce protein swelling, and this accords well with the theory. But salts can either decrease or increase swelling near the isoelectric point. In this case, anions are determinative, and they can be arranged in the following series according to the effect on swelling.

Anions which increase swelling:

$$NCS^- > I^- > Br^- > NO_3^- > ClO_3^-$$

Anions which decrease swelling:

$$Cl^- < CH_3COO^- < -OOC-CH_2-C(OH)(COO^-)-CH_2-COO^- <$$
$$< {}^-OOC-CH(OH)-COO^- < SO_4^{2-}$$

Anions have a different effect on swelling because they vary in their dissolving or, conversely, salting-out effect on proteins. The anion plays a special role in comparison with the cation because only the action of cations of alkali metals is reversible. All the polyvalent cations produce insoluble compounds, i.e., they cause the formation of an irreversible precipitate when they interact with $RCOO^-$ (an ordinary anion of macromolecular electrolytes).

Let us now see how the theory of membrane equilibrium can be used to explain the effect of pH and neutral electrolytes on protein viscosity. The saddle-like nature of the curve, which characterizes a change in the viscosity of a protein solution as a function of pH, is attributed to the ability of kinetic units of macromolecules in a solution to change their volume as a result of swelling or "unswelling". A change in the volume of particles in a solution should be accompanied by a respective change in viscosity. Loeb, who was the first to offer such an explanation, regarded a micelle as a kinetic unit in a protein solution. But at present, when it is proven that a polymer disintegrates to molecules in a solution, we should speak of the swelling of molecular coils rather than that of micelles. Such a view is in complete accord with the foregoing concepts of a change in the volume of molecular coils.

The effect which neutral electrolytes have on polyelectrolytic solutions can be explained by similar concepts. A change in viscosity greatly depends on the valency of the counterion and only inconsiderably depends on its position in the lyotropic series. Such a discrepancy in the effect of neutral electrolytes on gel swelling and that on solution viscosity occurs because the interaction between macromolecules is small in solutions; therefore the lyotropic effect, which makes the bonds between macromolecules either stronger or weaker, cannot be as pronounced in this case as in swelling.

Donnan's effect controls the distribution of electrolytes in the tissues of an organism and the origination of biopotentials. As we have seen in Chap. 3, Donnan's effect is also important to lyophobic systems where colloidal particles on which non-diffusing ions are adsorbed act as the membrane or the gel; this causes the non-uniform distribution of an electrolyte in a solution. Such distribution is especially expressed when sols are centrifuged (sol concentration effect) or suspensions settle (Pallmann-Wiegner suspension effect). In ultrafiltration, the Donnan effect may cause a non-uniform distribution of electrolytes in the ultrafiltrate and in the intermicellar liquid.

Electric properties of polyelectrolytic solutions. The electrokinetic potential can be calculated with certain accuracy by the Helmholtz-Smoluchowski or Henry equation only for colloidal particles whose dimensions are considerably greater than the thickness of the electric double layer. But for particles whose diameter is small in comparison with the thickness of this layer, several corrections must be made when the electrokinetic potential is being calculated, especially for electric relaxation. In addition if macromolecules are in the form of a loose coil in a solution, the motion of a medium through the loops of a coiled chain must be taken into account. Unfortunately, there is still no theory of electrophoresis for coiled macromolecules. Therefore, the electrophoretic mobility of not individual macromolecules, but of those adsorbed on sufficiently large particles of quartz or coal, or on oil droplets, is now determined. In this case, the electrokinetic potential can be easily measured by microelectrophoretic methods. Numerous investigations have shown that such a technique produces quite good results when the polymer layer covering a particle is sufficiently thick.

The values of the electrokinetic potential found for molecules of a polymer electrolyte in a solution are not accurate. The ionogenic groups of macromolecules and, consequently, the charges are arranged discretely along the length of a macromolecule, and we cannot speak here about the electric double layer in the ordinary sense of the word. It is more expedient to draw an analogy with individual ordinary ions which are surrounded with the Debye ionic atmosphere.

Therefore, the values of the electrokinetic potential that are found for solutions of macromolecular electrolytes only qualitatively characterize the electric properties of macromolecules in a solution.

Application of polyelectrolytes as flocculants. Polyelectrolytes are widely used in the national economy. Here, we will only consider their application as flocculants of suspensions having a polar (aqueous) medium and as ion-exchange resins.

As V. La Mer has shown, the most effective flocculating agents are polyelectrolytes having a sufficiently high molecular weight. In this case, polyelectrolytes should be used in very small amounts because their excess stabilizes suspensions.

Flocculation may occur because long chains of a polyelectrolyte molecule are adsorbed by one end on one suspension particle, and by the other, on another particle, forming a sufficiently strong bridge between particles. Flocculi consisting of more than two particles are formed in practice.

Another mechanism of flocculation is the formation of a bond between the active groups of polyelectrolyte molecules which are attached to suspension particles. Such flocculi can be easily separated from the aqueous medium because of their large dimensions.

Individual flocculi form a loose precipitate which is rather stable. If a solution of a polyelectrolyte capable of causing flocculation is added to a suspension of a powder or a fibre, the polyelectrolyte binds powder particles or individual fibres, as a result of which a bound system of practical interest can be obtained after drying. A polyelectrolyte has the greatest effect when it acts together with ordinary electrolytes. In this case, the polyelectrolyte should be introduced into a suspension before a low-molecular-weight electrolyte. Otherwise, suspension particles aggregate poorly and the precipitate is readily peptized.

The structure of a polyelectrolyte molecule, the nature of its active groups, and the ability of a polyelectrolyte to reside in a more or less unfolded state in an aqueous medium are very important to flocculation. Polyelectrolyte molecules, which are in a medium in the form of coils of low asymmetry, possess poor flocculating properties because some chain units that are screened by neighbouring active groups form intramolecular bonds and therefore cannot be adsorbed by suspension particles.

Various types of flocculants are now being produced on the industrial scale. One of the most widely used flocculants is the partially hydrolyzed polyacryl amide, which contains the $-NH_2$ and $-COOH$ groups. Hydrolysis which yields the $-COOH$ groups should be carried out in a way that only one-third of the $-NH_2$ groups would be hydrolyzed. When the degree of hydrolysis is higher, the polyacryl amide molecule acquires a negative charge which is so high that

the molecule is no longer adsorbed on the negatively charged particles of suspensions.

Polyelectrolytes are used as flocculants for coagulating circulating water in the coal industry and for extracting gold from wash and waste waters in the gold-extracting industry, thus reducing gold losses by 99.9 per cent. It is used in the paper industry for retaining the filler in paper and reducing fibre losses, and it is also employed for purifying waste waters. Flocculants are very important in agriculture for imparting the necessary properties to soil. An introduction of even very small amounts of flocculants into soil (0.02-0.05 per cent of the soil layer having a depth of 15 cm) reduces erosion, cross-links soil, making it easier to work the soil, and increases its moisture retentivity and water resistance. A polyelectrolyte introduced into soil is effective for about three years. Flocculants are very useful when they are added to the fine-grained clayey soils of the Central Asian Republics of the USSR. Therefore, the Tashkent State University (the school of K. S. Akhmedov, academician of the Uzbek SSR) is the centre where new flocculants are synthesized and their application is studied.

Application of polyelectrolytes as ionites. Ionites, or ion-exchange materials, are insoluble substances capable of exchanging their ions for other ions of the same sign which are present in the medium with which the ionite comes into contact. In Chap. 6, we have become acquainted with a typical representative of ionites, Permutite, which is used for extracting polyvalent cations (Ca^{2+}, Mg^{2+}, etc.) from water.

Synthetic resins are now used as ionites, and there are resins which are capable of exchanging both cations (cationites) and anions (anionites). The advantage of ion-exchange resins over ionites of other types is that they possess high mechanical strength, chemical stability, and great sorption (exchange) capacity. Ions can be exchanged by means of synthetic resins in the entire resin volume because dissolved ions penetrate freely through the cross-linked resin network.

Ion-exchange resins are obtained either by condensing or polymerizing monomers which contain active groups, or by introducing these groups into resins which have already been prepared. As the number of active groups in an ion-exchange resin increases, its exchange ability grows, but at the same time it becomes more capable of swelling and dissolving in water. As the number of cross-links in the structure of a resin increases, its ability to swell and dissolve decreases.

The dimensions of ionite grains range between 0.25 mm and 2.0 mm. The smaller are ionite grains, the more rapid is exchange, but also the more is the hydrodynamic resistance of a layer.

The exchange capacity of ionites is expressed by the number of gram-equivalents extracted by means of one gram of a dry ionite.

This capacity depends on the nature of active groups contained in an ionite, its structure, the nature of the ions undergoing exchange, the concentration of a solution and its pH. As pH increases, the

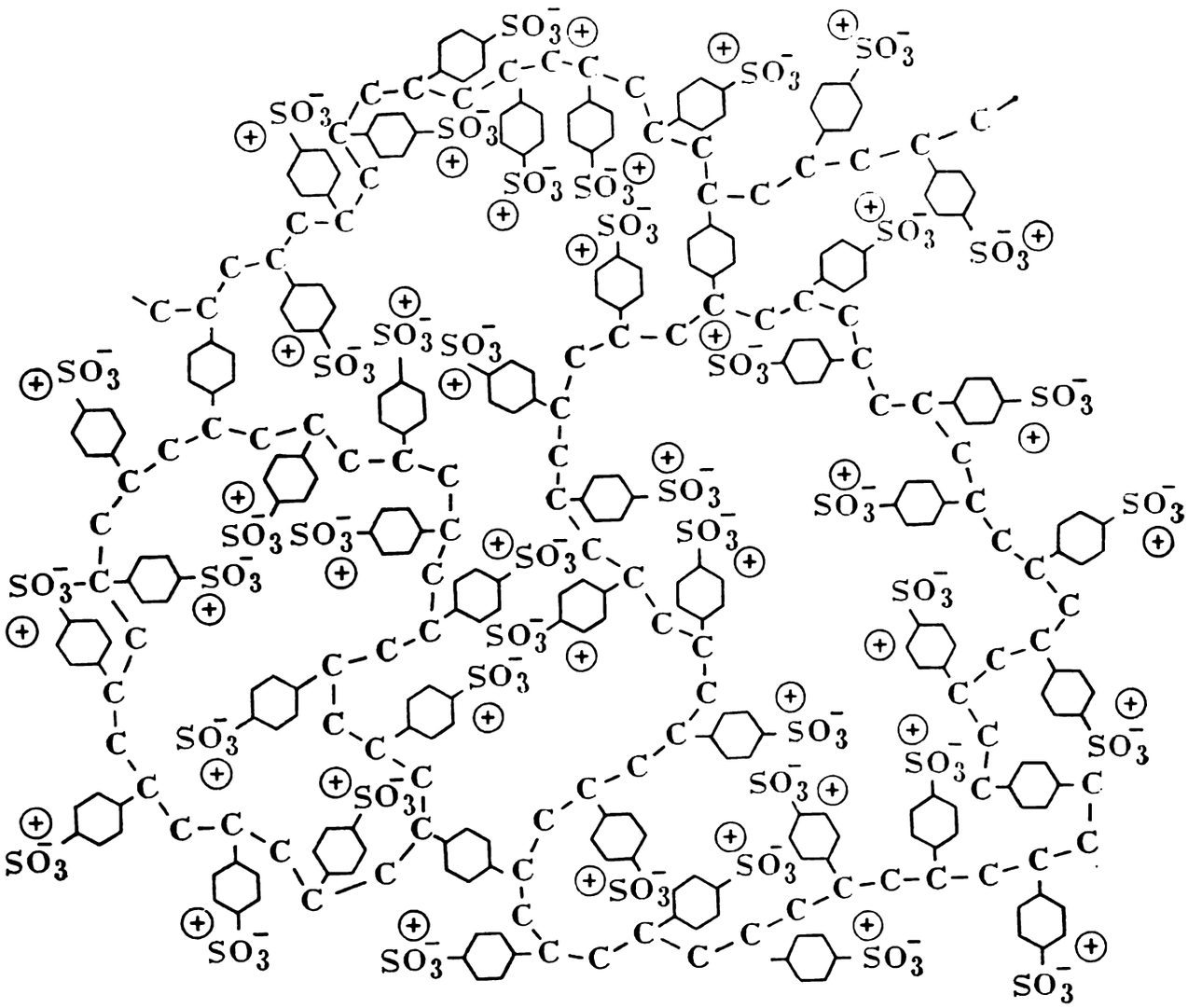

Fig. 14.16. Schematic structure of polysulphostyrene (the plus sign stands for cations being exchanged)

capacity of cationites grows, and that of anionites drops. As pH decreases, an opposite phenomenon occurs.The exchange capacity of modern ionites is 3-10 mg-equiv/g. After the ionite has been saturated, it is regenerated. To this end, cationites are treated with acid, and anionites, with alkaline solutions. Then, a regenerated ionite is washed and can be used again.

Cationites may contain $-SO_3H$, $-COOH$ and $-OH$ (phenol groups) as active groups. Even ordinary phenol-formaldehyde resins can be cationites. But the active hydroxyl group in such resins is weak, and therefore cationites containing the $-SO_3H$ group or the combination of groups $-SO_3H$ and $-OH$ are used. Fig. 14.16 schematically illustrates the structure of the simplest polysulphostyrene cationite.

Anionites may contain $-NH_2$, $=NH$ or $\equiv N$ as an active group. They began to be widely used only recently. An achievement in the field of anion-active resins is the synthesis of strongly basic anionites. They are used to remove weakly dissociating silicic acid, which is dangerous to boilers, from water. This was impossible earlier because the anionites known then had weakly basic properties.

Resins which selectively sorb individual ions, and amphoteric ionites which are suitable for separating amino acids and amphoteric elements have been synthesized recently. Ionites having optically active groups by means of which optical isomers can be separated are also beginning to be used.

Owing to the great achievements in the synthesis of ion-exchange resins, they are now used far outside water purification where they were originally employed. Ionites are used whenever it is necessary to remove, separate, and concentrate ions in solutions: in the energy-producing, chemical, food, pharmaceutical, metallurgical, and other industries. Ion-exchange resins are employed for separating ions which until now could not be separated by other methods, for instance, for separating rare earths, radioactive decay products, and so forth. Ionites are widely used in preparing pure reagents.

9. GELS

Solutions of macromolecular substances, like lyosols, lose their fluidity under certain conditions, i.e., they become gels. Gelation can occur spontaneously or when temperature changes, a solution is concentrated, and an electrolyte is added to it in an amount which is not too large. The structural viscosity of a system increases under the action of these factors, and a liquid becomes a gel, a system which exhibits several properties of a solid.

Gels and gelation are very important in medicine and biology because plants and animals are mainly composed of gels. The gelation of polymer solutions is of great importance also in technological processes. The formation of a glue layer in pastings, the gelation of pyroxylin, and the production of artificial fibre are all gelation processes. Several processes in the food and bread-baking industries are also connected with gelation. Clean rawhide, specially prepared animal hide which does not have a hair cover and from which leather is made in tanning, is gel.

Gelation. Gelation occurs because bonds originate between polymer molecules which are kinetic units in a solution. These bonds can exist for a short time, causing the origination of associates. However, if the average lifetime of bonds between macromolecules is very long (practically infinite), the formations do not disintegrate and to

a certain extent exhibit properties of a solid phase. Permanent bonds may originate between molecules in solutions of polymers as a result of interaction between the polar groups of macromolecules or between ionized ionogenic groups bearing electric charges of opposite sign. Sometimes chemical bonds are formed between macromolecules, e.g., when rubber is vulcanized in a solution.

Thus, gelation is the formation and gradual strengthening of a three-dimensional network in a system. When solutions of macromolecular substances become gels, bonds are formed not only at the

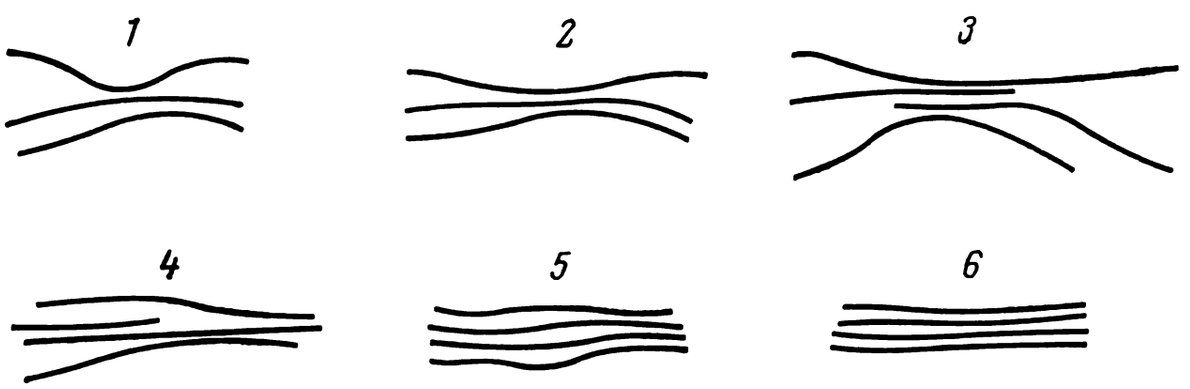

Fig. 14.17. Types of contacts of macromolecules in a gel (arranged in the order of the growth in their strength)

ends of kinetic units, as is the case when lyosols having elongated rigid particles become a gel, but between any regions of flexible macromolecules as long as they have groups which may interact with one another.

Individual regions of molecules that interact with one another become ordered when a gel is being formed, i.e., they orient parallel to one another because this reduces the free energy of a system. The degree of orientation depends on both the nature of a macromolecular substance and gelation conditions. Fig. 14.17 schematically illustrates various types of orientation of macromolecular regions in a gel, which are arranged in the order of their increasing strength.

There is a continuous transition from the simplest point contacts between macromolecules to crystallites, i.e., regions having an ordered crystalline structure. Since contacts may be of the most diverse nature in the same gel, it is expedient to use the concept of spectrum of molecular contacts for a given gel. This spectrum can be represented by a distribution curve which characterizes the fractional composition of contacts either by their strength or by their dimensions.

It is very likely that not only individual molecules, but also their bundles, can be structural units of the three-dimensional network of gels. Unfortunately, this so far has not been studied at all.

If the bonds between macromolecules are not too strong, mechanical action (stirring or shaking) can destroy the structure and a gel (just as a colloidal gel) becomes a liquid. When the external effect is

eliminated, the solutions obtained may spontaneously gelate again. But when molecules are combined into a continuous three-dimensional network by chemical bonds, strong mechanical effects irreversibly destroy a gel.

An elevation of temperature hinders gelation, provided irreversible chemical changes do not occur then in a system, because the micro-Brownian motion of segments becomes more intense and the number and lifetime of bonds between macromolecules consequently decrease. Conversely, a drop in temperature promotes gelation because the spectrum of contacts between macromolecules then expands and shifts towards higher strength. The solution-gel transition, like the gel-solution transition, occurs continuously with a change in temperature, i.e., there are no such temperatures as the crystallization and melting points here.

Sometimes, heating promotes gelation and, conversely, cooling causes the liquefaction of a system. Such a phenomenon is observed, for example, for methyl cellulose in water and cellulose nitrate in ethanol, being due to the negative temperature coefficient of a polymer solubility in a given solvent.

A growth in concentration always promotes the gelation of polymer solutions because then the frequency of collisions between macromolecules or between their parts becomes higher and the number of bonds per unit volume of a gel increases. But gelation can occur also in very diluted solutions owing to the elongated shape of macromolecules. At room temperature, for instance, an agar solution gelates already when its content of a dry substance is 0.2 per cent.

The greater the concentration, the higher is the temperature at which solutions of macromolecular substances become gels. For example, sufficiently concentrated (30-45 per cent) gelatin solutions are capable of gelating at about 30 °C whereas more diluted (10 per cent) solutions become gels at about 22 °C. Agar solutions gelate at even higher temperatures, and gels of higher stability than gelatin gels are then obtained. Conversely, rubber solutions gelate only at temperatures which are considerably lower than 0 °C. For example, a 3 per cent solution of natural rubber becomes a gel at —41 °C. Solutions of rubber gelate poorly because its molecules do not contain polar groups which can form a sufficiently strong bond when they come into contact with one another.

The volume of a system as a rule decreases on gelation. However, it increases when a silicic acid solution gelates. This increase, which occurs simultaneously with the polymerization of silicic acid, is caused by the liberation of water that had been chemically bound with SiO_2.

In some cases, gelation is accompanied by heat evolution. This may be caused by crystallite formation and the evolution of the crystalli-

zation heat. However, when solutions of macromolecular substances gelate, cooling curves do not show sharp maxima because the crystallization process is somewhat "blurred" since crystallites are not formed all at the same time.

The pH of a solution greatly affects the gelation ability of aqueous solutions of amphoteric macromolecular electrolytes, such as proteins. Gelation occurs best of all at pH values which correspond to the isoelectric point because the number of oppositely charged ionized groups along the length of a molecular chain is the same, and this helps to establish bonds between macromolecules. As pH changes towards either side of the isoelectric point, macromolecules assume a charge of the same sign, and this hinders the formation of bonds between them. When large amounts of an acid or an alkali are added, the extent of ionization of ionogenic groups decreases and the tendency to gelate increases again. In short, the gelation ability of protein solutions, like other properties, changes along a saddle-shaped curve with pH.

The action of neutral low-molecular-weight electrolytes on the gelation of protein solutions is directly opposite to that on swelling. Ions which promote swelling either retard gelation or make it impossible. Conversely, ions reducing the volume of a swollen gel promote gelation. Gelation, like swelling, is mainly affected by anions.

Besides the formation of intermolecular bonds, bonds between parts of the same macromolecule can also originate under certain conditions if it has several groups which are capable of interacting and the molecular chain is so flexible that its parts can come into contact as a result of thermal motion. In this case, *globular* or *corpuscular* gels are formed, according to V. Kargin and P. Zubov.

The formation of a globular gel, each globule of which consists only of a single macromolecule, is an extreme case. Globular gels can be formed under definite conditions also when two or more polymer molecules associate.

Globular gels are not precisely gels because they are capable of flowing. Since macromolecules here are compact coils and their parts cannot undergo micro-Brownian motion, the viscosity of such systems is even less than that of solutions of the same concentration in which macromolecules form loose coils.

An example of globular gels are systems prepared from 0.1 per cent solutions of cellulose nitrate in acetone when water is added to them. Stable gels containing up to 2 per cent of a dry residue can be obtained when such solutions are evaporated under vacuum. These systems possess several colloidal properties: they are capable of opalescing, the numerical concentration can be determined in them by means of an ultramicroscope, they obey the Schulze-Hardy rule when electrolytes are added to them, the electrokinetic potential of their particles sharply increases and the viscosity of a system

sharply decreases when a system is sufficiently diluted with water.

Another example of globular gels is a gelatin solution prepared under definite conditions. When a sufficiently concentrated gelatin solution is cooled below the temperature range of gel "melting", an ordinary, non-fluid gel is obtained as a result of the formation of intermolecular bonds. But if we cool a greatly diluted gelatin solution, in which molecules are far away from one another and thus mainly intramolecular bonds originate, it remains fluid. If such a solution is carefully concentrated without heating it above the temperature range of gel "melting", a globular gel is formed, and it remains fluid at the concentrations and temperatures which correspond to the existence of an ordinary gel. If the system is then heated, the intensification of micro-Brownian motion destroys the bonds between molecular regions, and the globular gel becomes a viscous solution of gelatin which then converts into an ordinary non-fluid gel on cooling. Thus, the transition of a globular gel to an ordinary one is a reversible process.

Similar systems are probably formed when a gelatin solution cools on intense stirring. Bundenberg de Jong showed as early as 1932 that a solution containing minute gelatin particles which are capable of sedimenting slowly, rather than a gel, is formed under these conditions. These particles could be compact coils of gelatin molecules.

Globular gels can exist for a very long time, i.e., they can be called stable systems. Thus, non-equilibrium solutions of macromolecular substances may also exist. This explains the fact that polymer solutions which have the same concentration but are prepared differently often differ in viscosity, osmotic pressure, and other properties.

Therefore, globular gels are intermediate in properties between polymer solutions and colloidal solutions.

Properties of gels. The most interesting properties of ordinary gels are their mechanical characteristics, particularly elasticity.

Solutions of polymers having extremely weak intermolecular bonds are capable of flowing, i.e., they react even to very weak shearing forces. But if the lifetime even of some contacts between macromolecules is very long, a gel becomes capable of resisting flow up to a definite value of shearing stress, and acts as an elastic solid under shearing conditions below this critical value. The value of critical shearing stress depends on the number and strength of molecular contacts.

The mechanical properties of gels are strongly affected by their concentration. Gels containing a small number of permanent intermolecular bonds per unit volume are very elastic. Conversely, gels having a large number of bonds between macromolecules are rather

poorly elastic because the greater the number of bonds between polymer chains, the less is the possibility of a change in the shape of macromolecules, i.e., the more rigid is the network formed.

The values of the critical shearing stress of agar solutions having different concentrations are given below.

Agar concentration, per cent	0.05	0.06	0.08	0.10	0.20	0.40
Critical shearing stress, g-force/cm^2	0.004	0.036	0.32	1.23	27	525

We can see that critical stresses increase very rapidly with concentration. A system exhibits gel properties when the content of agar in a solution is very low; in other words, the system is non-fluid.

At temperatures which are higher than the temperatures at which a gel "melts", neither diluted nor concentrated gels exhibit critical shearing stress. Non-gelating solutions, such as solutions of cellulose nitrate in acetone, do not exhibit critical shearing stress at any concentrations. They flow at the lowest shearing stress although very slowly because of their high viscosity.

Relaxation processes in gels occur at a higher rate than in polymer solutions because only individual, comparatively short chain segments can move in gels. Therefore, the elasticity of gels is always more pronounced than that of cross-linked solutions.

Some polymer gels possess well-defined thixotropic properties. The strength of the bonds between the macromolecules of these gels should be sufficiently low so that they could easily be destroyed under the action of shearing force. Moreover, such gels should have a sufficiently narrow spectrum of molecular contacts. Gels having a wide spectrum of such contacts do not exhibit thixotropy. Indeed, when the structure is being destroyed by mechanical action, most bonds are cleaved if the spectrum of molecular contacts is narrow, and then they are restored as a system is allowed to stand. This is the essence of thixotropy. But if the spectrum of contacts is wide, only a small number of bonds possessing the least strength are disrupted. A system then disintegrates into large pieces which cannot combine and form a structure having the initial value of critical shearing stress.

Since macromolecular systems are characterized by wide spectra of molecular contacts, thixotropy is exhibited only under special conditions which favour to narrow down the spectrum, e.g., on considerable dilution or at the initial stage of gelation when structures are not yet formed from oriented macromolecular parts.

A peculiar property of gels is their "memory" of how they were formed. Suppose one gel was prepared from a dilute gelatin solution and the other, from a concentrated one. Then, the gels were dried at low temperature to the same moisture content and were allowed

to swell in water. As a result, the first gel would swell much more than the second one because their internal structure, which originated when they were formed, was preserved to a certain extent when they were dried.

In many cases, gels can scatter light because crystallites or intermolecular contacts having a large area are formed in them. The presence of crystallites in the gels of macromolecular substances can be proven by X-ray diffraction analysis.

Interesting features are observed when particles of a colloidal dispersity or low-molecular-weight substances diffuse into a gel. Since gels whose concentration is not too high are three-dimensional networks having rather large meshes, small molecules or ions diffuse into them almost at the same rate as they do in a pure solvent, provided they do not react with the macromolecular substance of a gel. Diffusion into a gel, and not into a liquid, is sometimes used for determining diffusivity so as to exclude the effect of convection currents or jolts.

Low-dispersed systems cannot diffuse into a gel because particles do not penetrate into the meshes of a molecular network if they are larger than the mesh. In this case, the same conditions as in ultrafiltration originate especially because semipermeable membranes are usually typical gels.

Highly dispersed colloidal systems, and also polymer solutions whose molecules are not too large, diffuse into a gel at a different rate which depends on the dimensions of the diffusing kinetic units and the density of the molecular network of a gel.

Diffusion into gels takes place in dyeing and tanning, because the swollen fibre and clean rawhide are typical gels.

An interesting phenomenon is observed when a substance capable of forming an insoluble compound with a low-molecular-weight substance diffuses into a gel containing this substance. In this case, as R. Liesegang had found as far back as the last century, the precipitation often occurs only in definite regions of a system which alternate with those where a precipitate is not formed at all (the formation of "banded precipitates"). As a result, layers are formed if the substance diffuses into the depth of a gel, or rings are observed if the substance is applied at the centre of a gel surface and then diffuses parallel to the latter.

In the formation of such "banded precipitates", a gel apparently precludes the formation of convection currents in a system. This is confirmed by the fact that such precipitates may originate also in the diffusion of a low-molecular-weight substance into powders which are impregnated with a solution of another low-molecular-weight substance capable of producing a precipitate with the former.

Although many works have been dedicated to the study of Liesegang's layers and rings, it is still not quite clear how they are formed.

These layers and rings are often found in nature. For instance, the banded or layered patterns described above can be observed for some minerals (agates) and tissues (cross-striated muscles).

The electric conductivity of gels is similar to that of solutions from which they were obtained although the viscosity of a system sharply grows in gelation. This is because the three-dimensional network in a gel does not hinder the motion of comparatively small ions in a solvent; in other words, the "microviscosity" of a system remains unchanged when it gelates.

A specific property of some gels is that they can force out a liquid present in the meshes of a molecular network by means of some other liquid. If the second liquid mixes with the first one, the process can be effected by simply immersing a gel into the second liquid. If the liquids are immiscible, a third liquid which mixes with both of them must be used. For example, if water must be replaced by hydrocarbon in an aqueous gel, it is at first displaced with ethanol which can then be forced out with hydrocarbon that is miscible with it.

The gel in which the liquid medium has been replaced by a foreign liquid often becomes more rigid and does not shrink on drying. The molecular network of such a modified gel loses, as it were, elasticity and the ability to shrink when the medium is removed from it. In addition, as H. Hermans showed, a certain amount of liquid remains in such gels even after they have been thoroughly dried, and this is probably caused by steric factors. Molecular chains in a gel are packed very densely below a definite degree of swelling, and the molecules of a medium remain, as it were, occluded between them. Only molecules of a liquid soluble in a polymer can move between macromolecules which have closely approached one another. That is why the residues (traces) of liquids in polymer films can be removed from them with great difficulty.

Most gels found in plants and animals are anisotropic owing to the conditions of their formation. The anisotropy of prepared gels is usually caused by their non-uniform deformation when they are obtained or by non-uniform shrinkage when they are dried. An example is the gel obtained when a gelatin solution is dried on a glass plate. Shrinkage under such conditions can apparently occur only along the height of the gel film; as a result, gelatin macromolecules will orient mainly parallel to the plate plane. Of course, such properties of anisotropic gels as changes in the linear dimensions of a gel sample on swelling or shrinkage, refraction and absorption of light, birefringence, and also their mechanical properties, differ in the two directions.

The gels of macromolecular substances are very similar in properties to these substances when the gels contain a small amount of a solvent. Of course, a polymer which does not contain a solvent

is not a gel, but it can be obtained from a gel by drying and can be easily converted into a gel by swelling. Therefore, macromolecular substances capable of swelling are often considered to be the limiting state of a gel when a solvent is removed from it, and are known as *xerogels*, or "dry" gels ("xeros" means dry in Greek). Macromolecular substances incapable of swelling are known as *resins*. Examples of xerogels are dry gelatin, polystyrene, rubber, and cellulose fibre; an example of resins is bakelite.

Syneresis. Freshly prepared gels of macromolecular substances often undergo syneresis on standing: their volume decreases and the medium is spontaneously pressed out from an elastic gel. As a result, two macrophases, liquid and gelatinous ones, are formed, and the latter retains the shape of the vessel in which the original gel was. Syneresis is a very common phenomenon and can be observed not only in gels having a macromolecular network, but also, as we have seen in Chap. 10, in lyogels whose network consists of crystalline particles. Many phenomena of syneresis have been studied thoroughly by S. Lipatov.

Syneresis is caused generally because a system is still not in equilibrium when a gel is formed, and equilibrium continues to be established in it. For lyogels, these processes may consist in recrystallization. For macromolecular gels, they consist in the establishment of bonds between macromolecules, causing a further diminution in the gel volume. Syneresis may also result from the attainment of equilibrium in a gel when it cools, provided the macromolecular substance is not completely soluble in a medium. Syneresis can be also caused by chemical processes in the gel substance; for example, aqueous gels of cellulose xanthate undergo syneresis as xanthate decomposes.

Syneresis is characteristic of not only aqueous gels (e.g., gels of gelatin or starch), but also gels where the medium is an organic liquid (e.g., a rubber gel).

The limit to which a gel volume tends in syneresis depends on the concentration of a gel. Syneresis is the greater, the higher is the concentration of a solvent in the original gel. There is no definite dependence of the rate of syneresis on the concentration of the original gel. For example, at high concentrations, the syneresis of rubber gels is accelerated whereas that of starch or agar gels is retarded. According to Lipatov, the maximum gel volume in syneresis is the sum of the volumes of macromolecules and the volume of a solvent which is attached to a polymer by solvate bonds. A slight elevation of temperature promotes syneresis, facilitating molecular movement essential for gel shrinkage. But a gel may become a solution when temperature rises considerably. External pressure on a gel always promotes syneresis.

For gels of amphoteric proteins, maximum syneresis is observed at the isoelectric point because molecules bear an equal number of charges of opposite sign in such a state, and this favours the compression of the molecular network of a gel. Syneresis diminishes as the pH of a medium declines from the isoelectric point because molecular chains acquire a charge of the same sign, unfold, and repel one another.

The effect of low-molecular-weight electrolytes on gel syneresis is very complicated. As a rule, electrolytes which promote swelling reduce syneresis, and vice versa.

Syneresis depends on the dimensions of a gel sample: it is the less, the larger is the sample because the liquid which must be pressed out from larger gel samples in syneresis must overcome greater resistance.

Syneresis is very important in biology, medicine, and technological processes. It can be regarded as a favourable phenomenon when some resins are synthesized because a resin then spontaneously separates from a solvent. Syneresis is a favourable phenomenon also in the dairy industry because the production of pot cheese is based on it. It is an unfavourable phenomenon in the starch-syrup, marmalade, and some other food industries, and the technologist's task is to preclude it. Syneresis is extremely dangerous in the production of explosives, e.g., the separation of self-detonating nitroglycerin from a gel which is smokeless powder.

RECOMMENDED LITERATURE

A. TEXTBOOKS AND GUIDES

Rehbinder, P. A., *Konspekt obshchego kursa kolloidnoi khimii* (Synopsis of the General Course of Colloid Chemistry), II ed., Izd. MGU, Moscow, 1950.

Kruyt, H. R. (Ed.), *Colloid Science*, v. I, Elsevier Publ. Co., Amsterdam, 1952.

Sheludko, A., *Kolloidna khimiya* (Colloid Chemistry), Nauka i Izkustvo, Sofia, 1957.

Pasynsky, A. G., *Kolloidnaya khimiya* (Colloid Chemistry), II ed., Vysshaya shkola, Moscow, 1963.

Rehbinder, P. A., Fuchs, G. I. (Eds.), *Uspekhi kolloidnoi khimii* (Advances in Colloid Chemistry), Nauka, Moscow, 1973.

Fridrikhsberg, D. A., *Kurs kolloidnoi khimii* (A Course in Colloid Chemistry), Khimiya, Leningrad, 1974.

B. MONOGRAPHS AND REVIEWS

To Chapter 1

Rehbinder, P. A., *Novye problemy kolloidnoi khimii* (New Problems in Colloid Chemistry), Vestnik Akad. Nauk SSSR, 1955, Vol. 2, p. 8.

Voyutsky, S. S., Rehbinder, P. A., *O predmete i printsipakh postroyeniya kursa kolloidnoi khimii* (On the Subject and Principles of the Structure of the Course in Colloid Chemistry), Kolloid. zhur., 1956, Vol. 18, p. 253.

Rehbinder, P. A., *Razvitiye kolloidnoi khimii v SSSR za 40 let* (Development of Colloid Chemistry in USSR in the Last 40 Years), Usp. khim., 1957, Vol. 26, p. 320.

To Chapter 2

Shifrin, K. S., *Rasseyanie sveta v mutnoi srede* (Light Scattering in a Cloudy Medium), Gostekhteoretizdat, Moscow-Leningrad, 1951.

Lukyanovich, V. M., *Elektronnaya mikroskopiya v fiziko-khimicheskikh issledovaniyakh* (Electron Microscopy in Physico-chemical Investigations), Izd. Akad. Nauk SSSR, Moscow, 1960.

To Chapter 3

Figurovsky, N. A., *Sedimentometricheskii analiz* (Sedimentometric Analysis), Izd. Akad. Nauk SSSR, Moscow, 1948.

To Chapters 4-6

De Boer, J. H., *The Dynamical Character of Adsorption*, Clarendon Press, Oxford, 1953.

Gerasimov, Ya. I. (Ed.), *Kurs fizicheskoi khimii* (Course in Physical Chemistry), Vol. I, Khimiya, Moscow, 1970.

Lipatov, Yu. S., Sergeyeva, L. M., *Adsorbtsiya polimerov* (Polymer Adsorption), Naukova dumka, Kiev, 1972.

Deryagin, B. V., Krotova N. A., *Adgeziya* (Adhesion), Izd. Akad. Nauk SSSR, Moscow-Leningrad, 1949.

De Bruyne, N. A., Houwink, R. (Eds.), *Adhesion and Adhesives*, Elsevier Publ. Co., Amst., N.-Y.-Lond., 1951.

Voyutsky, S. S., *Autogeziya i adgeziya vysokopolimerov* (Autoadhesion and Adhesion of High Polymers), Rostekhizdat, Moscow, 1960.

Voyutsky, S. S., *Adgeziya. Entsiklopediya polimerov* (Adhesion. Encyclopedia of Polymers), Vol. I, Sovetskaya entsiklopediya, Moscow, 1972.
Deryagin, B. V., Krotova, N. A., Smilga, V. P., *Adgeziya tvyordykh tel* (Adhesion of Solids), Nauka, Moscow, 1973.
Berlin, A. A., Basin, V. E., *Osnovy adgezii polimerov* (Principles of Polymer Adhesion), Khimiya, Moscow, 1974.

To Chapter 7

Rehbinder, P. A. (Ed.), *Elektricheskiye svoistva kapillyarnykh sistem* (Electrical Properties of Capillary Systems), Izd. Akad. Nauk SSSR, Moscow-Leningrad, 1956.
Grigorov, O. N., Fridrikhsberg, D. A. (Eds.), *Elektropoverkhnostnye yavleniya v dispersnykh sistemakh* (Electrosurface Phenomena in Dispersed Systems), Nauka, Moscow, 1972.
Grigorov, O. N., *Elektrokineticheskiye yavleniya* (Electrokinetic Phenomena), Izd. LGU, Leningrad, 1973.
Dukhin, S. S., *Elektroprovodnost i electrokineticheskie svoistva dispersnykh sistem* (Electric Conductivity and Electrokinetic Properties of Dispersed Systems), Naukova Dumka, Kiev, 1975.
Dukhin, S. S., Derjaguin, B. V., in *Surface and Colloid Science*, ed. by E. Matijevic, V. 7, p. 1, Wiley, New York, 1974.

To Chapter 8

Berestnyova, Z. Ya., Kargin, V. A., *O mekhanizme obrazovaniya kolloidnykh chastits* (On the Mechanism of the Formation of Colloidal Particles), Usp. khim., 1955, Vol. 24, p. 249.
Rehbinder, P. A., *Sovremennye problemy kolloidnoi khimii* (Current Problems of Colloid Chemistry), Kolloid. zhur., 1958, Vol. 20, p. 527.
Rehbinder, P. A. *et al.*, *O termodinamicheskikh ravnovesnykh dvukhfaznykh dispersnykh sistemakh* (On the Thermodynamically Equilibrated Two-phase Dispersed Systems), Kolloid. zhur., 1970, Vol. 32, p. 480.

To Chapter 9

Deryagin, B. V., *Sovremennaya teoriya ustoichivosti liofobnykh suspenzii i solei* (Modern Theory of the Stability of Lyophobic Suspensions and Sols), Works of the Third All-Union Conference on Colloid Chemistry, Izd. Akad. Nauk SSSR, Moscow, 1956.
Voyutsky, S. S., Panich, R. M., *Agregativnaya ustoichivost dispersii polimerov i dzeta-potentsial* (Aggregate Stability of Polymer Dispersions and the Zeta-potential), Usp. khim., 1956, Vol. 25, p. 157.
Deryagin, B. V., Abrikosova, I. I., Lifshits, Ye. I., *Molekulyarnoye prityazheniye kondensirovannykh tel* (Molecular Attraction of Condensed Bodies), Usp. fiz. nauk, 1958, Vol. 64, p. 493.
Sonntag, H., Strenge, K., Koagulation und Stabilitat Disperser Systeme, Veb Deutscher Verlag der Wissenschaften, Berlin, 1970.
Deryagin, B. V. (Ed.), *Issledovaniya v oblasti poverkhnostnykh sil* (Investigations in the Field of Surface Forces), Vols. 1-5, Nauka, Moscow, 1961-1974.

To Chapter 10

Volarovich, M. P., *Issledovaniye reologicheskikh svoistv dispersnykh sistem* (Investigation of the Rheological Properties of Dispersed Systems), Kolloid. zhur., 1954, Vol. 16, p. 227.

Mikhailov, N. V., Rehbinder, P. A., *O strukturno-mekhanicheskikh svoistvakh dispersnykh i vysokomolekulyarnykh sistem* (On the Structural-mechanical Properties of Dispersed and Macromolecular Systems), Kolloid. zhur., 1955, Vol. 17, p. 107.
Akhmedov, K. S. (Ed.), *Strukturoobrazovaniye v dispersnykh sistemakh v prisutstvii polielektrolitov* (Structure-formation in Dispersed Systems in the Presence of Polyelectrolytes), Izd. FAN, Tashkent, 1970.
Efremov, I. F., in *Surface and Colloid Science*, ed. by E. Matijevic, V. 8, Wiley, New York, 1976.
Fuchs, G. I. (Ed.), *Issledovaniye po fiziko-khimii kontaktnykh vzaimodeistvii* (Investigation in Physico-chemical Contact Interactions), Bashkir Book Publishers, Ufa, 1971.

To Chapter 11

Amelin, A. G., *Teoreticheskiye osnovy obrazovaniya tumana pri kondensatsii para* (Theoretical Principles of Fog Formation in Vapour Condensation), III ed., Khimiya, Moscow, 1972.
Fuchs, N. A., *Mekhanika aerozolei* (Aerosol Mechanics), Izd. Akad. Nauk SSSR, Moscow, 1955.
Deryagin, B. V., *Aerozoli (dymy i tumany)* (Aerosols: Smokes and Fogs), Znaniye, Moscow, 1961.
Fuchs, N. A., *Uspekhi mekhaniki aerozolei* (Advances in Aerosol Mechanics), Izd. Akad. Nauk SSSR, Moscow, 1961.

To Chapter 12

Clayton, W., The Theory of Emulsions and Their Technical Treatment, J. a. A. Churchill Ltd., London, 1943.
Chukhrov, F. V., *Kolloidy v zemnoi kore* (Colloids in the Earth Crust), Izd. Akad. Nauk SSSR, Moscow, 1955.
Voyutsky, S. S., O prichinakh agregativnoi ustoichivosti emulsii (On the Causes of the Aggregate Stability of Emulsions), Usp. khim., 1961, Vol. 30, p. 1237.
Sherman, P., Emulsion Science, Academic Press, New York, 1968.

To Chapter 13

Stupel, H., Synthetische Wasch und Reinigungsmittel, Konradin Verlag Robert Kohlhammer, Stuttgart, 1957.
Schwartz, A. M., Perry, J. W., Berch, J., *Surface-active Agents and Detergents*, Academic Press, New-York, 1958.
Rehbinder, P. A., *Poverkhnostno-aktivnye veshchestva i ikh primeneniye* (Surfactants and Their Application), Khim. nauka i prom., 1959, Vol. 5, p. 554.
Schönfeld, N., Oberflächenaktive Anlagerungsprodukte des Äthylenoxyds, Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1959.
Shinoda, K., Nakagawa, T., Tamamushi, B., Isemura, T., Colloidal Surfactants, Academic Press, New-York & London, 1963.

To Chapter 14

Voyutsky, S. S., *Rastvory vysokomolekulyarnykh soyedinenii* (Solutions of Macromolecular Compounds), II ed., Goskhimizdat, Moscow, 1960.
Tager, A. A., *Physical Chemistry of Polymers*, Mir Publishers, Moscow, 1972.
Morawetz, H., Macromolecules in Solution, Interscience Publ., New York, 1965.

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